A TEXT-BOOK OF

INORGANIC CHEMISTRY

VOLUME I.

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A TEXT-BOOK OF
INORGANIC CHEMISTRY.

EDITED BY

J. NEWTON FRIEND, D.Sc., F.I.C., Ph.D.,

Carnegie Gold Medallist.

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Frontispiece.

THE PERIODIC TABLE.

PERIODS.		GROUP 0.	GROUP I.	GROUP II.	GROUP III.	GROUP IV.	GROUP V.	GROUP VI.	GROUP VII.	GROUP VIII.
First short period		He 4·00	H 1·008 Li 6·94	Gl 9·1	B 11·0	C 12·005	N 14·01	O 16·00	F 19·0	
Second short period		Ne 20·2	Na 23·00	Mg 24·32	Al 27·1	Si 28·3	P 31·04	S 32·06	Cl 35·46	
First long period	Even series	A 39·88	K 39·10	Ca 40·07	Sc 44·1	Ti 48·1	V 51·0	Cr 52·0	Mn 54·93	Fe 55·84 Co 58·97 Ni 58·68
	Odd ,,	...	Cu 63·57	Zn 65·37	Ga 69·9	Ge 72·5	As 74·96	Se 79·2	Br 79·92	
Second long period	Even series	Kr 82·9	Rb 85·45	Sr 87·63	Y 88·7	Zr 90·6	Cb 93·1	Mo 96·0	...	Ru 101·7 Rh 102·9 Pd 106·7
	Odd ,,	...	Ag 107·88	Cd 112·4	In 114·8	Sn 118·7	Sb 120·2	Te 127·5	I 126·92	
Third long period	Even series	X 130·2	Cs 132·81	Ba 137·37	THE RARE EARTH METALS	...	...	...	...	... ...
	Odd ,,	...	...	...		...	...	...	...	
Fourth long period	Even series	...	...	...		...	Ta 181·5	W 184·0	...	Os 190·9 Ir 193·1 Pt 195·2
	Odd ,,	...	Au 197·2	Hg 200·6	Tl 204·0	Pb 207·20	Bi 208·0	...	...	
Fifth long period		Nt 222·4	...	Ra 226·0	...	Th 232·4	...	U 238·2	...	... ...
Formulæ of oxides Formulæ of hydrides		...	R_2O RH	RO RH_2	R_2O_3 RH_3	RO_2 RH_4	R_2O_5 RH_3	RO_3 RH_2	R_2O_7 RH	RO_4
Volume in this series of text-books.		1	2	3	4	5	6	7	8	9

* The International Atomic Weights for 1917 are adopted in this Table.

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BY
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D.Sc. (B'ham.), Ph.D (Würz.), Carnegie Gold Medallist;
Temporary Lieutenant with H. M. Forces.

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B.Sc. (Lond.), A.R.C.S., D.I.C. D.Sc. (Lond.), M.Sc. (B'ham.)

Part II.—THE INERT GASES.

BY
H. VINCENT A. BRISCOE,
D.Sc. (Lond.), A.R.C.S., D.I.C.

With Frontispiece, Plate, and 88 other Illustrations.

THIRD EDITION.

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GENERAL INTRODUCTION TO THE SERIES

DURING the past few years the civilised world has begun to realise th advantages accruing to scientific research, with the result that an eve increasing amount of time and thought is being devoted to various branche of science.

No study has progressed more rapidly than chemistry. This scienc may be divided roughly into several branches: namely, Organic, Physical Inorganic, and Analytical Chemistry. It is impossible to write any singl text-book which shall contain within its two covers a thorough treatment o any one of these branches, owing to the vast amount of information that ha been accumulated. The need is rather for a series of text-books dealing mor or less comprehensively with each branch of chemistry. This has alread been attempted by enterprising firms, so far as physical and analytica chemistry are concerned; and the present series is designed to meet th needs of inorganic chemists. One great advantage of this procedure lies i the fact that our knowledge of the different sections of science does no progress at the same rate. Consequently, as soon as any particular par advances out of proportion to others, the volume dealing with that sectio may be easily revised or rewritten as occasion requires.

Some method of classifying the elements for treatment in this way i clearly essential, and we have adopted the Periodic Classification with slight alterations, devoting a whole volume to the consideration of the elements in each vertical column, as will be evident from a glance at the scheme in the Frontispiece.

In the first volume, in addition to a detailed account of the Elements of Group 0, the general principles of Inorganic Chemistry are discussed. Particular pains have been taken in the selection of material for this volume, and an attempt has been made to present to the reader a clear account of the principles upon which our knowledge of modern Inorganic Chemistry is based.

At the outset it may be well to explain that it was not intended to write a complete text-book of Physical Chemistry. Numerous excellent works have already been devoted to this subject, and a volume on such lines would scarcely serve as a suitable introduction to this series. Whilst Physical Chemistry deals with the general principles applied to all branches of theoretical chemistry, our aim has been to emphasise their application to Inorganic Chemistry, with which branch of the subject this series of text-books is exclusively concerned. To this end practically all the illustrations to the laws and principles discussed in Volume I. deal with inorganic substances.

Again, there are many subjects, such as the methods employed in the accurate determination of atomic weights, which are not generally regarded as forming part of Physical Chemistry. Yet these are subjects of supreme importance to the student of Inorganic Chemistry, and are accordingly included in the Introduction.

Hydrogen and the ammonium salts are dealt with in Volume II., along with the Elements of Group I. The position of the rare earth metals in the Periodic Classification has for many years been a source of difficulty. They have all been included in Volume IV., along with the Elements of Group III., as this was found to be the most suitable place for them.

Many alloys and compounds have an equal claim to be considered in two or more volumes of this series, but this would entail unnecessary duplication. For example, alloys of copper and tin might be dealt with in Volumes II. and V. respectively. Similarly, certain double salts—such, for example, as ferrous ammonium sulphate—might very logically be included in Volume II. under ammonium, and in Volume IX. under iron. As a general rule this difficulty has been overcome by treating complex substances, containing two or more metals or bases, in that volume dealing with the metal or base which belongs to the highest group of the Periodic Table. For example, the alloys of copper and tin are detailed in Volume V. along with tin, since copper occurs earlier, namely in Volume II. Similarly, ferrous ammonium sulphate is discussed in Volume IX. under iron, and not under ammonium in Volume II. The ferrocyanides are likewise dealt with in Volume IX.

But even with this arrangement it has not always been found easy to adopt a perfectly logical line of treatment. For example, in the chromates and permanganates the chromium and manganese function as part of the acid radicles and are analogous to sulphur and chlorine in sulphates and perchlorates; so that they should be treated in the volume dealing with the metal acting as base, namely, in the case of potassium permanganate, under potassium in Volume II. But the alkali permanganates possess such close analogies with one another that separate treatment of these salts hardly seems desirable. They are therefore considered in Volume VIII.

Numerous other little irregularities of a like nature occur, but it is hoped that, by means of carefully compiled indexes and frequent cross referencing in the texts of the separate volumes, the student will experience no difficulty in finding the information he requires.

Particular care has been taken with the sections dealing with the atomic weights of the elements in question. The figures given are not necessarily those to be found in the original memoirs, but have been recalculated, except where otherwise stated, using the following fundamental values:—

Hydrogen = 1·00762.
Sodium = 22·996.
Potassium = 39·100.
Silver = 107·880.
Carbon = 12·003.
Nitrogen = 14·008.

Oxygen = 16·000.
Sulphur = 32·065.
Fluorine = 19·015.
Chlorine = 35·457.
Bromine = 79·916.
Iodine = 126·920.

By adopting this method it is easy to compare directly the results of earlier investigators with those of more recent date, and moreover it renders the data for the different elements strictly comparable throughout the whole series.

Our aim has not been to make the volumes absolutely exhaustive, as this would render them unnecessarily bulky and expensive; rather has it been to contribute concise and suggestive accounts of the various topics, and to append numerous references to the leading works and memoirs dealing with the same. Every effort has been made to render these references accurate and reliable, and it is hoped that they will prove a useful feature of the series. The more important abbreviations, which are substantially the same as those adopted by the Chemical Society, are detailed in the subjoined list.

In order that the series shall attain the maximum utility, it is necessary to arrange for a certain amount of uniformity throughout, and this involves the suppression of the personality of the individual author to a corresponding extent for the sake of the common welfare. It is at once my duty and my pleasure to express my sincere appreciation of the kind and ready manner in which the authors have accommodated themselves to this task, which, without their hearty co-operation, could never have been successful. Finally, I wish to acknowledge the unfailing courtesy of the publishers, Messrs Charles Griffin & Co., who have done everything in their power to render the work straightforward and easy.

J. NEWTON FRIEND.

September 1916.

PREFACE TO THE SECOND EDITION OF VOLUME I.

PARTS I. AND II.

As only two years have elapsed since the first edition of this volume received publication, and as, moreover, during this period investigations in pure science have been greatly retarded by the war, it was felt to be neither necessary nor desirable to institute any fundamental change in this second edition. The Authors have therefore in the main confined their alterations to—

1. Correction of such verbal or other mistakes in the first edition as have been brought to their notice.
2. Revision and addition of such physical and other data as seemed desirable in view of the latest published researches.
3. Addition of references to the most recent literature dealing with the various subjects under discussion.
4. Re-writing the section on Valency in considerably greater detail.

In conclusion, the Authors desire to thank their readers for the kind reception accorded to the first edition of this volume.

J. N. F.
H. F. V. L.
W. E. S. T.
H. V. A. B.

November 1916.

PREFACE TO THE THIRD EDITION OF VOLUME I.

PARTS I. AND II.

In view of the fact that very few investigations in pure science have been carried out since the second edition of this volume was issued, it has been judged desirable to publish this third edition without making any alterations in the text.

J. N. F.
H. F. V. L.
W. E. S. T.
H. V. A. B

June 1, 1918

PREFACE TO PART I.

(FIRST EDITION).

THE preparation of this Introductory Part has proved to be a task of peculiar difficulty. At the outset we would emphasise the fact that our aim has not been to write a complete text-book of Physical Chemistry. Numerous excellent works have already been devoted to this subject, and we felt that a volume on such lines would scarcely serve as a suitable introduction to this series. Whilst Physical Chemistry deals with the general principles applied to all branches of theoretical chemistry, we have been desirous of emphasising their application to Inorganic Chemistry, with which branch of the subject this series of text-books is exclusively concerned. To this end practically all the illustrations to the laws and principles discussed deal with inorganic substances.

Again, there are many subjects, such as the methods employed in the accurate determination of atomic weights, which are not generally regarded as forming part of Physical Chemistry. Yet these are subjects of supreme importance to the student of Inorganic Chemistry, and are accordingly included in this Introduction.

We have attempted in the opening chapter to present to the reader a concise account of the Fundamental Laws upon which the modern study of Inorganic Chemistry rests, and to show how they have been confirmed by modern experimental research. In the two succeeding chapters the general Properties of Elements and Compounds are discussed, whilst Chapter IV. is devoted to the study of the various methods of determining Molecular Weights and the discussion of the values sometimes obtained. Chemical Change and the Properties of Acids, Bases, and Salts form the subject-matter of Chapters V. and VI.

The determination of the Atomic and Equivalent or Combining Weights of the Elements is dealt with in Chapter VII. Several pages are here devoted to a discussion of the best means of carrying out the necessary chemical processes involved, and attention is drawn to the numerous experimental errors that must be guarded against if results of the highest accuracy are to be obtained. By way of illustration, a full account is given of the methods employed by Richards and his collaborators in determining the atomic weight of lithium, by precipitation of the chloride with silver nitrate. As a second example we have chosen Guye's researches on the atomic weight of nitrogen, as it involves the determination of the densities of highly purified gases.

These descriptions will, we hope, enable the student to realise to what a high degree of accuracy it is possible to attain in modern chemical and physical research.

A short account of Series Lines in Spectra, the Zeeman Effect, and the connection between Spectra and Atomic Weights is also included in Chapter VII. Lack of space has prevented us from dealing with the general subject of

Spectroscopy in this volume in Chapter II., but an account of Absorption and Phosphorescence Spectra will be found in Volume IV. of this series, in connection with the Rare Earths.

The final chapter is devoted to the Classification of the Elements and a consideration of their Valency.

It seems impossible to find a perfectly logical order of sequence for such a wide range of subjects, and some of our readers may think that the material might have been more suitably arranged. In reply we can only say that the present scheme was decided upon after very careful consideration of the whole problem, and although we realise its imperfections, we believe it to be on the whole a fairly satisfactory one. Since, moreover, the book is addressed to students who already possess an elementary knowledge of chemistry and physics, the occasional departures from logical order should not create any difficulties. By means of the full index and frequent cross-referencing in the text, the student should experience no difficulty in finding the information he requires.

A considerable amount of entirely new material has been introduced into the different chapters, and is here presented and discussed, we believe, for the first time in book form.

In an attempt to cover so wide a field in the space afforded by some 300 pages, it is obviously impossible to deal exhaustively with the whole of the subjects. Our aim, therefore, has been to contribute concise and suggestive accounts of the various topics, and to append numerous references to the leading works and memoirs dealing with the same. Every effort has been made to render these references accurate and reliable, and it is hoped that they will prove a useful feature of the work. The abbreviations are substantially the same as those adopted by the Chemical Society.

The various sources from which we have culled information are, we believe, fully acknowledged in the text, but we take this opportunity of expressing our indebtedness to the Geological Department of the Imperial College of Science and Technology for the drawings upon which most of our crystallography diagrams are based, and to Mr Eric Sinkinson, of the Imperial College of Science and Technology, for executing several of the other diagrams.

J. NEWTON FRIEND.
H. F. V. LITTLE.
W. E. S. TURNER.

August 1914.

PREFACE TO PART II.

(FIRST EDITION)

IN the second part the Author has endeavoured to present a full and clear account of the present state of our knowledge of the inert gases of the atmosphere, and especially of those points which are of interest to chemists.

Hitherto the most complete account in English of these gases has been given by Ramsay in *The Gases of the Atmosphere*, and by Travers in *The Study of Gases*, and the Author would here like to express his indebtedness to these works.

The present work differs materially in several ways from its predecessors (*e.g.* in dealing in detail with the evidence for and against the common belief in the inertness of the elements of Group 0), and it has been the aim throughout to draw a clear line of demarcation between what is definitely known concerning the inert gases and what is uncertain or speculative.

Particular care has been taken to furnish numerous and accurate references to the leading literature on the subject, so that readers wishing to study any of the sections in further detail may be able to do so with the minimum of trouble.

In conclusion, the Author wishes to thank Dr J. Newton Friend and Mr H. F. V. Little, B.Sc., for their kindly criticism of his MS., and to acknowledge the assistance of these gentlemen and of Miss R. K. Stevenson, B.Sc., and Mr W. Jevons, A.R.C.S., B.Sc., in correcting the proofs.

The plate of spectra has been reproduced from photographs taken in the Astrophysical Laboratory of the Royal College of Science, and the Author's thanks are due to Professor A. Fowler, F.R.S., for kind assistance in its preparation.

H. V. A. BRISCOE.

August 1914.

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LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Sci.	American Journal of Science and Arts
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Annalen der Chemie.
Ann. Chim.	Annales de Chimie (1719-1815, and 1914+).
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, l'Agriculture, à la Pharmacie, et à la Biologie.
Ann. Chim. applicata	Annali di Chimica applicata.
Ann. Chim. Phys.	Annales de Chimie et de Physique (1816-1913).
Ann. Falsif.	Annales des Falsifications.
Ann. Min.	Annales des Mines.
Ann. Phys.	Annales de Physique (1914+).
Ann. Physik	Annalen der Physik.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arkiv Kem. Min Geol.	Arkiv for Kemi, Mineralogi och Geologi.
Atti R. Accad. Lincei	Atti della Reale Accademia Lincei.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Ber. deut. physikal. Ges.	Berichte der deutschen physikalischen Gesellschaft.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. Sci. Petrograd	Bulletin de l'Académie Impériale des Sciences de Petrograd.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. d'Enc. p. l'Ind. nationale	Bulletin de la Société d'Encouragement pour l'Industrie nationale.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. U.S. Geol. Survey	Bulletin of the United States Geological Survey.
Centr. Min.	Centralblatt für Mineralogie, Geologie, und Palæontologie.
Chem. Ind.	Die chemische Industrie.
Chem. News	Chemical News.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Dingl. poly. J.	Dingler's polytechnisches Journal.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Intern. Zeitsch. Metallographie	International Zeitschrift für Metallographie.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie, und Palæontologie.
Jahrb. Radioaktiv. Electronik	Jahrbuch der Radioaktivitat und Electronik.
Jahresber.	Jahresbericht über die Fortschritte der Chemie.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Chim. phys.	Journal de Chimie physique.
J. Coll. Sci. Tokyo	Journal of the College of Science, Tokyo.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physique	Journal de Physique.
J. Physical Chem.	Journal of Physical Chemistry.

ABBREVIATED TITLE.	JOURNAL.
J. prakt. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers	Journal of the Society of Dyers and Colourists.
J. Washington Acad. Sci	Journal of the Washington Academy of Sciences.
Kolloid-Zeitsch.	Kolloid-Zeitschrift.
K. Svenska Vet.-Akad. Handl.	Kongl. Svenska Vetenskaps-Akademiens Handlingar.
Mém. Acad. Roy. Belg.	Mémoires de l'Académie Royale de Belgique.
Met. Chem. Eng.	Metallurgical and Chemical Engineering.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte fur Chemie und verwandte Theile anderer Wissenschaften.
Nova Acta Soc. Upsala.	Nova Acta Regiæ Societatis Scientiarum Upsaliensis.
Pharm. Zentr.-h.	Pharmaceutische Zentralhalle.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phys. Review	Physical Review.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Pogg. Annalen	Poggendorff's Annalen der Physik und Chemie.
Proc. Chem Soc.	Proceedings of the Chemical Society.
Proc. Amer. Acad.	Proceedings of the American Academy of Arts and Sciences.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam, Proceedings (English Version).
Proc. Manchester Lit. Phil. Soc.	Proceedings of the Manchester Literary and Philosophical Society.
Proc. Roy. Soc.	Proceedings of the Royal Society of London.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Schweigger's J.	Schweigger's Journal fur Chemie und Physik (continued as Journal fur praktische Chemie).
Sci. Proc. Roy. Dubl Soc.	Scientific Proceedings of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss Berlin	Sitzungsberichte der Koniglich-Preussischen Akademie der Wissenschaften zu Berlin
Sitzungsber. K. Akad. Wiss. Wien	Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften, Wien.
South African J Sci	South African Journal of Science.
Tech. Papers, Bur. Stand.	Technical Papers, Bureau of Standards, Washington.
Tonind. Zeit.	Tonindustrie Zeitung.
Trans. Amer. Cer. Soc	Transactions of the American Ceramic Society.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Chem. Soc.	Transactions of the Chemical Society.
Trans. Eng. Cer. Soc.	Transactions of the English Ceramic Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Inst. Mng. Eng.	Transactions of the Institute of Mining Engineers.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen.
Wied. Annalen	Wiedemann's Annalen der Physik und Chemie.
Zeitsch. anal. Chem.	Zeitschrift fur analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift fur angewandte Chemie.
Zeitsch. anorg. Chem	Zeitschrift fur anorganische Chemie.
Zeitsch. Chem. Ind. Kolloide	Zeitschrift für Chemie und Industrie des Kolloide (continued as Kolloid-Zeitschrift).
Zeitsch. Elektrochem.	Zeitschrift fur Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift fur Krystallographie und Mineralogie.
Zeitsch. physikal. Chem.	Zeitschrift fur physikalische Chemie, Stochiometrie und Verwandtschaftslehre.
Zeitsch. wiss. Photochem.	Zeitschrift fur wissenschaftliche Photographie, Photophysik, und Photochemie.

VOLUME I. PART I.

INTRODUCTION
TO
MODERN INORGANIC CHEMISTRY

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A TEXT-BOOK OF INORGANIC CHEMISTRY.

VOL. I. PART I.

AN INTRODUCTION TO MODERN INORGANIC CHEMISTRY.

CHAPTER I.

THE FUNDAMENTALS OF CHEMICAL SCIENCE.

Introductory; Chemical and Physical Changes.—The various changes that bodies undergo may be divided into two classes, termed **Physical Changes** and **Chemical Changes.** Physical changes affect only a few of the properties of bodies concerned; their consideration forms the subject of Physics. Chemical changes are of a more profound nature; the bodies concerned in them disappear, and their places are taken by other bodies possessing other properties.

It is not easy to draw a sharp distinction between these two classes of changes, but the nature of the differences between them may be indicated by a few oft-quoted examples. Consider, for example, a piece of sulphur. It is a pale yellow, solid body of low specific gravity. When rubbed with a cloth, it acquires the property of attracting scraps of paper and other light objects, *i.e.* it becomes electrified. It still retains its other properties unchanged, however, and can be made to lose its new property of electrification without bringing about a change in any of its other properties. The electrification of sulphur is therefore a physical change. When the sulphur is heated, it easily melts, forming a yellow liquid; on cooling, it again passes into the solid state. It is not so easy to understand why this change should be classed as physical; but for reasons that will appear later, change of state is usually regarded as a physical phenomenon.

When the piece of sulphur is brought into contact with a flame, a profound change occurs. The sulphur catches fire, and burns with a pale blue flame; eventually it disappears completely. At the same time, a characteristic smell is noticed, indicating that something has been produced that was not present initially. In fact, a portion of the surrounding air disappears with the sulphur, and a colourless gas (sulphur dioxide) with a powerful odour is produced. When sulphur burns, therefore, a chemical change occurs.

Mercury or quicksilver is a mobile, silver-white, shining liquid of high specific gravity and boiling-point. When a little mercury is heated in air for a considerable time at a temperature slightly below its boiling-point, the occurrence of a chemical change is made evident by the appearance of a new red body on the surface of the mercury. Here again the air takes part in the change. If the experiment is carried out in a closed vessel, the red body eventually ceases to be formed, and the gas which remains (mainly nitrogen) is found to differ from ordinary air since it extinguishes a lighted match.

When the new red body (mercuric oxide) is heated in a tube, it darkens considerably in colour, and ultimately becomes almost black. This is only a physical change, and, on cooling, the body resumes its former appearance. A chemical change occurs, however, when the body is more intensely heated. Mercury is observed on the cool parts of the tube, and a colourless gas (oxygen) is produced that is easily shown to differ from ordinary air since a splint of wood that just glows in air bursts into flame when plunged into the gas. If the heating is prolonged sufficiently, the red body completely disappears.

A chemical change also takes place when a little mercury and sulphur are rubbed together vigorously in a mortar. Much of the mercury and sulphur disappear, and a new black body (mercuric sulphide) makes its appearance.

Chemical changes are a matter of common observation in daily life; the burning of coal, oil, and gas, and the decaying of dead vegetable and animal matter are familiar processes which are readily seen to come under this heading. The science of Chemistry is concerned with the elucidation of the laws relating to these phenomena.

The laws of chemical combination will be discussed in this chapter, and the classification of chemical changes, etc., considered later (see Chap. V.).

The Conservation of Mass.—The quantitative study of chemical changes has led to the formulation of a fundamental law, which applies to all changes, both physical and chemical. This is the **Law of the Conservation of Mass**; it may be stated in the form that *the mass of a system is unaltered by any change that occurs within it*, or that *in a chemical change the total mass of the substances that disappear is equal to the total mass of the substances produced.* For example, referring to one of the changes already mentioned, the mass of the mercuric sulphide formed is precisely equal to the sum of the masses of the mercury and sulphur that disappear. In the chemical change that takes place when sulphur burns, the law does not, at first sight, appear to hold; but this is due to the fact that two of the three bodies concerned in the change are colourless gases. When the diminution in the mass of the surrounding air is determined, and also the mass of the gaseous substance produced, it is found that the latter exceeds the former by exactly the mass of the sulphur that disappears.

The discovery that, in the formation and decomposition of mercuric oxide, the combined masses of the mercury and oxygen taking part in the changes are equal to the mass of the mercuric oxide, is due to Lavoisier, and is of great historical interest to the chemist. In fact, it was by Lavoisier[1] that the Law of the Conservation of Mass was first clearly perceived and stated. It is not difficult to realise that such a law should have escaped the attention of the early chemists, unacquainted as they were with the existence of different gases, and unaccustomed to placing any reliance on measurements of mass (or weight) in interpreting the nature of chemical changes.

Although it is difficult to realise how chemistry could exist as an exact science if the Law of the Conservation of Mass were not true, it must nevertheless be borne in mind that the law rests upon a purely experimental basis. Its truth is assumed in all quantitative chemical work, and the assumption has never led to contradictory conclusions. The indirect evidence of the validity of the law is supplemented by the results of direct experiments, especially undertaken with the object of putting the law to the test. Fifteen different reactions were studied by Landolt[1] with the greatest care, the method employed being briefly as follows. The materials used in a reaction were contained in the limbs of a sealed, inverted U-tube, which, after being weighed against a similar counterpoise, was righted in order to mix the materials and cause the reaction to take place. The weight was then observed again. The contents of the counterpoise were then mixed, and a third weighing made. The conclusion finally reached by Landolt was that in these reactions there was no difference between the masses of the systems before and after chemical change greater than could be attributed to error in weighing. The latter was only 0·03 mgrm., and the masses of the reacting systems were of the order of 300 grms.

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[1] Lavoisier, *Œuvres*, vol. i. p. 101.

Additional evidence of the accuracy of the law is contained in the data supplied by Stas[2] in his syntheses of silver bromide and iodide; by Morley[3] and Noyes[4] in their syntheses of water; by Edgar[5] in his syntheses of hydrogen chloride, and by Gray[6] in his analyses of nitric oxide.[7] Hence, if any changes in mass do occur in chemical reactions, they must be far too small to be of any practical importance to the chemist; and the Law of the Conservation of Mass may be classed among the exact laws.

The Conservation of Energy.—Corresponding to the principle of the conservation of mass there is another fundamental physical principle concerning *energy*. The general statement of the principle of the **Conservation of Energy** is as follows:—[8]

The total energy of any material system is a quantity which can neither be increased nor diminished by any action between the parts of the system, though it may be transformed into any of the forms of which energy is susceptible.

The energy content of the products of a chemical change is, in general, however, different from that of the starting materials, and this is manifested as a rule by the evolution or absorption of heat during the reaction. This phenomenon will be discussed in some detail in a later chapter (Chap. V. p. 161).

Although the total quantity of energy in the universe is constant, it is not all *available* to man for the purpose of doing work. During every transformation some energy is converted into heat, which becomes uniformly diffused and is therefore generally regarded as being unavailable inasmuch as further change is deemed impossible. *If this be granted*, it is clear that the total available energy is steadily diminishing, while the unavailable energy is as steadily increasing, and a time must come when all the available energy of the universe will become unavailable, the universe itself becoming a uniformly hot, inert mass. This doctrine is known as the **Dissipation of Energy.** The fact, however, that we are not at present acquainted with any method of rendering uniformly diffused heat available does not necessarily imply that it is actually incapable of being rendered so; and it may well be that, by processes not yet understood, the so-called unavailable energy is being continuously transformed into available energy, so that the universe may never reach the state of equilibrium and inertness referred to above.[1]

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[1] Landolt, *Sitzungsber. K. Akad. Wiss. Berlin*, 1893, 301; 1906, 266; 1908, 354; *Zeitsch. physikal. Chem.*, 1893, **12**, 1; 1906, **55**, 589; *Chem. News*, 1906, **93**, 271; review by Guye in *J. Chim. phys.*, 1908, **6**, 625.

[2] Stas, *Œuvres complètes*, Brussels, 1891, vol. i. pp. 308, 419.

[3] Morley, *Smithsonian Contributions*, 1895, **29**, No. 980.

[4] Noyes, *J. Amer. Chem. Soc.*, 1907, **29**, 1718.

[5] Edgar, *Phil. Trans.*, 1909, A, **209**, 1.

[6] Gray, *Trans. Chem. Soc.*, 1905, **87**, 1601.

[7] See also Manley, *Proc. Roy. Soc.*, 1912, A, **87**, 202; *Phil. Trans.*, 1912, A, **212**, 227.

[8] Clerk Maxwell, *Matter and Motion* (Society for Promoting Christian Knowledge, 1882), p. 60.

Mixtures and Homogeneous Substances. — Simple inspection reveals the fact that certain substances do not possess identical properties throughout. Thus, the existence of three different materials in *granite* is immediately obvious when a piece of that substance is examined. By breaking up the granite into small fragments, these three materials become mechanically separated; and a further examination discloses differences in density, crystalline form, etc., between the three materials.

On the other hand, a piece of the mineral known as *Iceland Spar* shows no obvious differences in properties in different places, neither does it do so when reduced to fragments. On the contrary, a careful study of the specific physical properties[2] of the fragments shows that they are all specimens of the same substance.

A substance, such as Iceland Spar, which ordinary observation does not show to consist of different parts, is said to be **homogeneous**; the minutest portion that can be mechanically detached possesses the same specific physical properties as does the substance in bulk. A homogeneous mass is also referred to as a **phase.** Materials, such as granite, which possess different properties in different parts, are said to be **heterogeneous**, or are called **mixtures**. Chemistry is primarily concerned with the study of homogeneous substances, and in the following pages the term "substance" will be used to denote "homogeneous substance."

Solutions.—It will be seen subsequently that substances may be divided into three groups. The substances belonging to one of these groups are in many respects analogous to mixtures; accordingly, some chemists restrict the application of the term "substance" to the other two groups only,[3] excluding this particular group, which comprises **solutions.**

The significance of the term "solution" may be best explained by means of an example. If a small quantity of common salt be added to water, it disappears, and, either as the result of long standing or of stirring, a homogeneous liquid mass is obtained, termed a *solution* of salt in water. If further additions of small amounts of salt be made, they too disappear, until eventually a limit is reached, after which further quantities of salt cease to disappear and remain in the solid state. Thus, salt and water may be brought together in any proportions comprised between certain limits, with the production of a homogeneous liquid. Moreover, continuous variations in the relative amounts of salt and water are associated with continuous changes in the physical properties of the resulting liquid. In this instance, the inferior limit to the amount of salt is zero; the superior limit is found to vary both with temperature and pressure.

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[1] This point has been fully discussed by H. S. Shelton (*The Oxford and Cambridge Review*, 1912, No. 17, pp. 158-180) to whose memoir the reader is referred for further details.

[2] It is a fundamental law that when a number of *bodies* are found to agree exactly in a few of their properties, further examination shows them to agree exactly in all their properties; such bodies are said to be specimens of one and the same *substance*. The "substance" is therefore a conception derived by abstracting the properties common to all its specimens. By *properties* or specific properties is here understood those, such as colour, hardness, specific gravity, etc., which are the same in all parts of the bodies, excluding the *attributes* of mass, shape, etc., which differentiate the different specimens and the *conditions* of pressure, temperature, etc., which may be altered at will.

[3] *Cf.* Ostwald, *The Principles of Inorganic Chemistry*, trans. by Findlay, 3rd edition (Macmillan & Co., 1908).

Although the constituents of the solution, salt and water, cannot be mechanically detached, as in the case of a heterogeneous mass, the separation can nevertheless be effected by physical means, namely, by causing one of them to undergo a change of state. For instance, by supplying heat to the solution the water may be converted into vapour and thereby separated from the salt, which remains in the solid state. Or, by cooling the solution, water may be continuously removed as ice, until, in this instance, after the remaining solution has reached a certain concentration, further cooling results in the production of a heterogeneous solid mass of ice and salt.

A **solution**, then, may be defined as *a homogeneous mass, the composition of which may undergo continuous variation (between the limits of its existence), and which may be separated into two (or more) homogeneous substances by processes involving change of state.* This definition does not restrict solutions to any particular state of matter. Accordingly there may be gaseous, liquid, and solid solutions; and a substance is classed as a solution when, by processes involving change of state, it can be separated into a number of other substances A, B, C, . . ., and forms one member of a series of substances the compositions of which range over all the possible proportions of A, B, C, . . . comprised between certain limits.

Solutions are usually classed as mixtures, being referred to as "homogeneous mixtures" in order to distinguish them from the class of mixtures previously mentioned; occasionally, however, they are described as compounds of variable composition.[1]

The subject of solution is dealt with in a later chapter (see Chap. III.).

Elements.—Various substances have been already mentioned that do not fall under the heading of solutions, *e.g.* mercury, sulphur, oxygen, mercuric oxide, mercuric sulphide, sulphur dioxide, salt, and water. They are therefore "substances" in the narrowest sense of the word. From what has been already said concerning these substances, it will be recognised that mercury, sulphur, and oxygen are in a way simpler substances than mercuric sulphide, mercuric oxide, and sulphur dioxide, for each of the last three substances is built up from two of the preceding. In fact, mercury, oxygen, and sulphur are representatives of the simplest class of substances—namely, those which have never yet been separated into dissimilar parts, by any processes whatsoever. Such substances are called **elements**; *an element is a distinct species of matter that has not yet been shown to be composite.* All other substances are composed of two or more elements.

The term "element" was originally used in its modern significance by Boyle (1627-91), and was clearly defined by Lavoisier in his *Traité de chimie* (1789). Centuries before the time of Boyle the word was in use; but the ancients and the alchemists regarded the "elements" not as material substances, but rather as the fundamental qualities of different substances.

About eighty elements are known at the present day; a list of their names, symbols, and atomic weights will be found on p. 25. Helium, neon, argon, krypton, xenon, niton, hydrogen, oxygen, nitrogen, fluorine, and chlorine are gaseous at common temperatures; bromine and mercury are liquids; the remaining elements are solids in ordinary circumstances. Only a few occur in nature in the free state. Some elements are much more abundant than others; the following table gives, according to F. W. Clarke, the average composition of terrestrial material (including the earth's crust, the ocean, and the atmosphere):—

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[1] *Cf.* Kahlenberg, *Outlines of Chemistry* (Macmillan & Co., 1909).

Element.	Per cent.	Element.	Per cent.	Element.	Per cent.
Oxygen	49·8	Potassium	2·28	Barium	0·09
Silicon	26·1	Hydrogen	0·95	Manganese	0·07
Aluminium	7·34	Titanium	0·37	Strontium	0·03
Iron	4·11	Chlorine	0·21	Nitrogen	0·02
Calcium	3·19	Carbon	0·19	Fluorine	0·02
Sodium	2·33	Phosphorus	0·11	Remaining elements	0·48
Magnesium	2·24	Sulphur	0·11		

A distinction should be drawn between the terms "**element**" and "**elementary substance**," the elements being the different species of matter of which elementary substances are made.[1] Thus, oxygen and mercury in the free state are elementary substances, while mercuric oxide (*vide supra*, p. 4) contains the two elements mercury and oxygen. This distinction of terms is not always maintained, and very little ambiguity is thereby occasioned; but it is often convenient, for an element may exist in the free state in more than one form. There are, for instance, two elementary substances corresponding to the one element oxygen. This phenomenon is termed **allotropy**; it is exhibited by numerous elements, and will be discussed later (p. 64).

The elements may be divided into two classes, **metals** and **non-metals**. The division is merely one of convenience, and is imperfect, for no hard and fast line of demarcation between the two classes can be drawn. The *non-metals* include the gaseous elements and bromine, sulphur, selenium, tellurium, phosphorus, arsenic, carbon, silicon, boron, and iodine; the *metals* comprise the remaining elements. The names of the metals and non-metals discovered during the last hundred years usually end in *-ium* and *-on* respectively; the names "selenium" and "tellurium" do not conform to this rule, since these substances were originally classed among the metals.

Gold, silver, iron, copper, tin, and lead were known to the ancients mercury was also known in very early times. The metals as a class are distinguished by certain physical properties. They are opaque in bulk, possess a characteristic lustre, and are (more or less) malleable and ductile they are good conductors of heat and electricity. The formation of alloys should also be mentioned (see pp. 110, 116). Each of the metals, however, does not exhibit all of these properties in a high degree; for example, zinc, bismuth, and antimony are brittle, and hence were regarded throughout the Middle Ages as semi-metals. Moreover, some of these properties are possessed by certain non-metals; iodine and tellurium are lustrous, whilst silicon, graphite and, at a red heat, boron readily conduct electricity. Formerly, al metals were considered to possess high densities, an idea that was abandoned when Davy isolated sodium and potassium and demonstrated their metallic character. The metallic nature of mercury was admitted in 1759, when it was first frozen.

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[1] This distinction was clearly indicated by Mendeléeff (*Annalen Suppl.*, 1872, 8, 133).

The non-metals differ widely in their physical properties. A number of them are gases; the solid non-metals are brittle, possess low densities, and usually have no lustre and very little power of conducting heat or electricity.

The metals and non-metals are distinguished not only by their physical, but also by their chemical properties. A discussion of the latter, however, must be postponed till later (see Chap. VI.).

The difficulty of drawing a dividing line between metals and non-metals is clearly shown by the existence of an alternative method of classifying the elements, which divides them into three groups, namely, *non-metals*, *metalloids*, and *metals*. A metalloid is an element which, although it resembles a metal in most characteristics, yet lacks some one or more of the features which typical metals generally present. Usually, the metalloids possess the form or appearance of metals, but are more closely allied to the non-metals in their chemical behaviour. The following elements are included in the metalloids:[1] hydrogen, tellurium, germanium, tin, titanium, zirconium, arsenic, antimony, bismuth, vanadium, columbium, tantalum, molybdenum, tungsten, and uranium. The name "metalloid" was introduced by Erman and Simon in 1808[2] to describe an element that resembled a true metal. In 1811, however, Berzelius employed the term as synonymous with "non-metal," and at the present time it is still used by some chemists in that sense. It is perhaps best, therefore, to avoid the use of the word "metalloid" altogether.

Although to the chemist the elements are the ultimate forms of matter from which other substances are built up, it does not follow that they do not possess a complex structure. In recent years elements have been discovered which *spontaneously* break up into other elements.[3] These changes, however, which proceed at definite rates in accordance with a simple law, would seem to be beyond the power of the chemist to control.

Compounds: Law of Fixed Ratios: Law of Multiple Proportions.—Two of the three groups into which substances may be divided have now been dealt with—namely, solutions and elementary substances,—and the third group, exemplified by mercuric oxide, mercuric sulphide, sulphur dioxide, salt, and water, now calls for attention. Substances of this group do not possess the properties of solutions, but nevertheless they are composite, in the sense that each contains at least two elements. They are called **chemical compounds**, or simply **compounds**. Each of the above-mentioned compounds contains two elements only.

The elements present in a compound are said to be in a state of *chemical combination*; and the *chemical composition* of the compound is a statement, usually expressed in percentages, of the relative proportions in which the elements occur. It may be stated at once that, as would be expected, bodies which possess identical physical properties are also found to possess identical chemical compositions;[4] the converse, however, is not true.

Turning now to a consideration of the compositions of binary compounds,

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[1] See Tilden, *Introduction to Chemical Philosophy* (Longmans & Co.), 10th edition, 1901.

[2] Erman and Simon, Gilbert's *Annalen*, 1808, 28, 347.

[3] *Cf.* Vol. III. (Radium); Vol. V. (Thorium); Vol. VII. (Uranium).

[4] Recent researches indicate that there may be exceptions to this. See p. [illegible]; also Soddy, *The Chemistry of the Radio-elements* (Longmans & Co.), 2 parts, 1911–14.

i.e. compounds containing only two elements, the question naturally arises as to the number of compounds that two elements are capable of forming. The answer that experiment furnishes is very simple. *Two elements unite with one another in a limited number of definite ratios, separated by finite intervals.*[1] This may be called the **Law of Fixed Ratios.** As a rule, the number of ratios is quite small, varying in different cases from one to five or six; but the combining ratios of carbon and hydrogen are very numerous. To take an example, carbon and oxygen unite to form three gaseous compounds, known as carbon suboxide, monoxide, and dioxide, in which the carbon and oxygen are in the ratios of 1 to 0·8889, 1 to 1·333 and 1 to 2·667 respectively.[2] Any gaseous body that contains carbon and oxygen only, but not in one of the three ratios just quoted, proves to be a mixture; and even if its composition is represented by either of the last two ratios, the possibility of its being a mixture (of some or all of the oxides and oxygen) is not excluded.

The Law of Fixed Ratios became definitely established as a result of the classical controversy between Proust and Berthollet[3] which lasted from 1802 to 1808; and subsequent work has served to demonstrate the exactness of the law. Although the work of Proust was sufficient to satisfy his contemporaries as to the correctness of the law, his analytical results were not particularly accurate, and partly, perhaps, for this reason, he failed to observe a remarkable connection that exists between the various ratios in which two elements are found to unite. The combining ratios already given for carbon and oxygen will serve to illustrate the nature of this connection. It will be noticed that

$$0·8889 : 1·333 : 2·667 :: 2 : 3 : 6,$$

i.e. the weights of oxygen that separately unite with unit weight of carbon, are in the ratios of small whole numbers. This is only one illustration of an experimental generalisation known as the **Law of Multiple Proportions,** which may be stated in the following manner:—

When two elements unite in more than one ratio, the several weights of one element that combine with a fixed weight of the other element are in the ratios of simple integers.

The name of Dalton is usually associated with this law. Its history is very interesting, for it is almost certain that Dalton first of all deduced the law as a necessary consequence of his Atomic Theory, and afterwards found in the compositions of olefiant gas and marsh gas on the one hand, and carbon monoxide and dioxide on the other, experimental confirmation of his views.

The early analyses, the results of which constituted the experimental basis of the Law of Multiple Proportions, were naturally somewhat crude and inaccurate; the perfection of analytical methods, effected since the law was enunciated, has enabled chemists to submit the law to a more rigorous examination, and thereby to demonstrate its exactness. One example will suffice. Guye and Bogdan (*vide infra*, p. 279), in their gravimetric analyses of nitrous oxide, obtained the result—

$$\text{nitrogen} : \text{oxygen} :: 1·75100 : 1;$$

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[1] See Hartog, *Nature*, 1894, 50, 149.

[2] Carbon suboxide cannot be formed *directly* from its elements. A fourth oxide of carbon is known, but is solid at ordinary temperatures (H. Meyer and Steiner, *Ber.*, 1913, 46, 813; Jarrard, *Proc. Chem. Soc.*, 1913, 29, 106).

[3] Miss Freund, *The Study of Chemical Composition* (Cambridge University Press), 1904, chap. v.; see also Hartog, *Nature*, 1894, 50, 149.

the analyses of nitric oxide effected by Gray[1] led to the result—

nitrogen : oxygen :: 0·87563 : 1;

and lastly, Guye and Drouginine (*vide infra*, p. 254) obtained the following result for the composition of nitrogen peroxide—

nitrogen : oxygen :: 0·43782 : 1

Now,

1·75100 : 0·87563 : 0·43782 :: 3·9994 : 2 : 1·0000,

and the three last numbers are in the ratios

4 : 2 : 1

within the limits of experimental error.

Law of Equivalent Ratios: Combining Weights.—Continuing the inquiry further, another problem presents itself. Is there any connection between (i.) the ratios in which two elements occur in compounds which also contain other elements, and (ii.) the ratios in which the same two elements combine to form binary compounds? Here, again, a very simple relationship has been observed. The ratios (i.) and (ii.) are all related to one another in a simple numerical fashion. One or two instances may be quoted. The compound nitrosyl chloride contains nitrogen, oxygen, and chlorine, and the ratio of the nitrogen to the oxygen has been found by Guye and Fluss (see p. 254) to be 0·8754 to 1. This is practically identical with the ratio already given for nitrogen to oxygen in nitric oxide. The ratios of lead to sulphur in lead sulphide and lead sulphate were shown[2] by Berzelius in 1812 to be equal. Later, Stas showed that the ratios of silver to iodine in silver iodide and silver iodate were exactly equal, and obtained similar results for silver bromide—silver bromate and silver chloride—silver chlorate.

The Law of Multiple Proportions only constitutes, however, part of a far more comprehensive law, dealing with the compositions of all compounds. This law may now be considered, binary compounds being the first to receive notice.

Both chlorine and bromine unite with almost all the other elements, forming substances the compositions of which have in many cases been very accurately determined. The following results are typical:—

(i.) One part of silver combines with 0·328668 of chlorine[3] or with 0·740785 of bromine;[4] and 0·328668 : 0·740785 :: *1* : *2·2539*.

(ii.) One part of potassium combines with 0·906908 of chlorine[5] or with 2·04408 of bromine;[6] and 0·906908 : 2·04408 :: *1* : *2·2539*.

(iii.) One part of mercury unites with 0·353491 of chlorine[7] or with 0·796610 of bromine;[8] and 0·353491 : 0 796610 :: *1* : *2·2536*.

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[1] Gray, *Trans. Chem. Soc.*, 1905, 87, 1601.

[2] Berzelius, *vide infra*; *cf.* Ostwald's *Klassiker*, No 35.

[3] Richards and Wells, *Carnegie Institution Publications*, Washington, 1905, No. 28; *Amer. Chem. Soc.*, 1905, 27, 459.

[4] Baxter, *J. Amer. Chem. Soc.*, 1906, 28, 1322.

[5] Richards and Stähler, *Carnegie Institution Publications*, Washington, 1907, No. 69; *Amer. Chem. Soc.*, 1907, 29, 623.

[6] Richards and Mueller, *Carnegie Institution Publications*, Washington, 1907, No. 69; *Amer. Chem. Soc.*, 1907, 29, 639.

[7] Easley, *J. Amer. Chem. Soc.*, 1910, 32, 1117.

[8] Easley and Brann, *J. Amer. Chem. Soc.*, 1912, 34, 101.

An extraordinary regularity is noticeable in the above figures. The ratio chlorine : bromine is a constant.[1] Bearing in mind that some elements form several chlorides and bromides, the compositions of which conform to the Law of Multiple Proportions, it may therefore be stated that the quantities of chlorine and bromine that unite with a fixed quantity of one element are either in the same ratio as are the quantities of those two elements that unite with a fixed quantity of any other element, or else the ratios are simply related.

The preceding generalisation is found to hold not only for chlorine and bromine, but for any two elements whatsoever. The general statement of the law, known as the **Law of Equivalent Ratios**, may be expressed in the following manner:—

The ratios of the masses of two elements that combine with one and the same mass of a third element bear a simple numerical relationship to the ratios of the masses of the two elements that combine either with one and the same mass of any other element or with one another.

For example, in nitrogen peroxide one part of nitrogen is combined with 2·28404 of oxygen,[2] whilst in nitrogen sulphide one part of nitrogen is combined with 2·28901 of sulphur.[3] But,

$$2{\cdot}28404 : 2{\cdot}28901 :: 1 : 1{\cdot}0022,$$

and according to the law, there should be a simple numerical relationship between this ratio and the ratios in which oxygen and sulphur combine together. Now, in sulphur dioxide the ratio of oxygen to sulphur is 1 to 1·0020,[4] which is practically equal to the preceding ratio.

The law may be expressed more concisely by introducing the notion of combining weights or chemical equivalents. *The combining weight or chemical equivalent of an element is the number of parts by weight of the element that combine with 8 parts by weight of oxygen.*[5] In view of the existence of the Law of Multiple Proportions, it is clear that an element may have a number of combining weights, which will be in the ratios of simple integers. The Law of Equivalent Ratios may now be stated in the following manner, and called the **Law of Combining Weights**:—

Elements combine with one another in the ratios of simple multiples of their combining weights.

In discussing this law, binary compounds alone have been so far considered, but it will be clear from what has been already stated at the beginning of this section (p. 11) that this restriction may be removed, and that *the compositions of all compounds conform to the Law of Combining Weights.*

The determination of combining weights is a matter of fundamental importance. According to the preceding law, the combining weight of an element may be determined either directly with reference to oxygen, or indirectly with reference to another element of known combining weight. The latter method is employed more often than the former, and thus it happens that the combining weights of certain elements are extremely important, since they are so often utilised in calculating the combining weights of the others. These "fundamental" combining weights include those of chlorine, bromine, iodine, hydrogen, nitrogen, carbon, sulphur, sodium, and potassium.

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[1] The data for the chlorides and bromides of sodium, calcium, silicon, titanium, etc (Clarke, *vide infra*, p. 13), lead to the same value for the ratio.

[2] Guye and Drouginine, *vide infra*, p. 13.

[3] Burt and Usher, *Proc. Roy. Soc.*, 1911, **A**, 85, 82.

[4] Deduced from the ratios oxygen : tellurium dioxide :: 0·200485 : 1 (Gutbier, *Annalen*, 1905, 342, 266), and tellurium dioxide : sulphur dioxide : : 1 : 0·40136 (Baker and Bennett, *Trans. Chem. Soc.*, 1907, 91, 1849).

[5] The value 8 is chosen for oxygen as being one-half its atomic weight, which i arbitrarily fixed as 16 (*vide infra*, p. 231).

The precautions necessary in the accurate measurement of combining weights are fully dealt with later, in Chap. VII. For the calculation of combining weights from all the most reliable data, the student is referred elsewhere.[1] A few simple calculations, which will serve to illustrate the Law of Combining Weights, may not, however, be out of place.

Since 1·0076 parts of hydrogen combine with 8 of oxygen to form water,[2] the combining weight of *hydrogen* is *1·0076*. One part of hydrogen unites with 35·1935 of chlorine.[3] Now, 1 : 35·1935 : : 1·0076 : 35·461, and hence the combining weight of *chlorine* is *35·461*. Since, further, 0·328668 parts of chlorine combine with 1 of silver,[4] and 0·328668 : 1 : : 35·461 : 107·893, the combining weight of *silver* is *107·893*.

According to Baxter,[5] one part of iodine combines with 0·849906 of silver, and as 0·849906 : 1 : : 107·893 : 126·947, the combining weight of *iodine* is *126·947*. In an oxide of iodine, however, Baxter and Tilley found that the oxygen and iodine were in the ratio of 8 to 25·3827 ;[6] hence another combining weight of *iodine* is *25·3827*. Now, 25·3827 : 126·947 : : *1 : 5·0013*, so that the two combining weights of iodine are in the ratio of one to five within the limits of experimental error.

From the ratio, quoted on p. 11, of potassium to chlorine in potassium chloride, the combining weight of *potassium* is *39·101*, if that of chlorine is 35·461. The sum is therefore 74·562. Now, potassium chlorate differs from potassium chloride in containing oxygen, and is readily converted into potassium chloride by loss of oxygen. In this change, 1·64382 parts of potassium chlorate yield 1 of potassium chloride ;[7] but 1 : 0·64382 : : 74·562 : 48·004, and the last number is practically equal to 48, or six times the combining weight of oxygen. Hence, in potassium chlorate, for each combining weight of potassium there is one of chlorine and six of oxygen.

Some idea may be given of the concordance that has been obtained between the various values, arrived at by different methods, for the combining weights of certain elements. The preceding proportion is equivalent to 1 : 0·64382 : : 74·555 : 48, which indicates that the sum of the combining weights of chlorine and potassium is 74·552. The ratios already given for potassium to chlorine, silver to chlorine, and silver to iodine then lead to the values *39·097*, *35·458*, *107·884*, and *126·936* for the combining weights of potassium, chlorine, silver, and iodine, which only differ by 0·004, 0·003, 0·009, and 0·011 from the values already deduced in another way.

The Law of Combining Weights is thus seen to be exact: that is to say, no deviations are observed greater than those for which experimental error may be responsible. Its enormous importance will be at once obvious; the study of chemical composition would be unmanageable but for this law.

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[1] Clarke, *A Recalculation of the Atomic Weights*, Smithsonian Collections, Washington, vol. liv., No. 3 (1910).

[2] Morley, *Smithsonian Contributions*, 1895, 29, No. 980.

[3] Edgar, *Phil. Trans.*, 1909, A, 209, 1.

[4] *Vide supra*, p. 11.

[5] Baxter, *J. Amer. Chem. Soc.*, 1910, 32, 1591.

[6] Baxter and Tilley, *J. Amer. Chem. Soc.*, 1909, 31, 201 ; Baxter, *vide supra*.

[7] Stähler and Meyer, *Zeitsch. anorg. Chem.*, 1911, 71, 378.

Since a chemical reaction is one in which a number of substances, elementary or compound, disappear, being replaced by a number of others, it is not difficult to see that the following law must hold for chemical reactions: *the masses of substances, elementary or compound, that are equivalent in any one reaction,* i.e. *which unite with or interact with the same amount of a third substance, are identical with or bear a simple numerical relation to the masses equivalent in any other reaction, including that of combination with each other.*

It was from the results of experiments on the interactions of elements and compounds that the Law of Equivalent Ratios was deduced by Richter at the end of the eighteenth century.[1] Richter showed, and correctly explained the fact, that when two neutral salts interact, the resulting salts are still neutral; and also deduced, from the fact (previously observed by Bergmann) that when one metal is precipitated from a solution of a neutral salt by another metal the resulting solution is likewise neutral, that the masses of two metals which neutralise the same mass of an acid also combine with equal masses of oxygen. Further, Richter showed that the quantities of various bases (basic oxides) which neutralise a fixed quantity of one acid are in the same ratios as the quantities of the bases which neutralise a fixed quantity of another acid.

Richter's experimental results were only rough approximations to the truth; the first experiments having any pretensions to accuracy which served to demonstrate the truth of the Law of Equivalent Ratios were made by Berzelius in 1811–12,[2] some years after Dalton had promulgated his Atomic Theory.[3] The degree of accuracy of the law was subsequently made the subject of a special investigation by Stas,[4] and from the results of his extremely careful and accurate experiments he concluded that the law is exact.

The Law of Combining Volumes.—The laws previously discussed deal with the regularities that are noticed among the masses or weights of substances concerned in chemical changes. The law which expresses the volume relationships observed in chemical reactions involving gases was discovered by Gay-Lussac. In 1805 Gay-Lussac and Humboldt[5] noticed that when hydrogen and oxygen unite to form water, the respective volumes of these gases that enter into combination are in the ratio of two to one[6] when measured at the same temperature and pressure. The simplicity of this relationship led Gay-Lussac to the study of other gaseous reactions, and in 1808 he enunciated the **Law of Combining Volumes**, which may be stated in the following manner: *Whenever gases unite, they do so in proportions by volume (at the same temperature and pressure) which can be represented by*

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[1] Richter, *Anfangsgründe der Stochiometrie*, 1792–4; *Ueber die neueren Gegenstände der Chemie*, 1792–1807.

[2] Berzelius, Gilbert's *Annalen*, 1811, 37, 249, 415; 38, 161, 227; 1812, 40, 162, 235; 42, 276. See Ostwald's *Klassiker*, No. 35.

[3] *Cf.* Miss Ida Freund, *opus cit.*, chap. vii.

[4] Stas, (1) "Recherches sur les rapports réciproques des poids atomiques," *Bull. Acad. Roy. Belg.*, 1860, [ii.], 10, 208; *Œuvres complètes*, Brussels, 1894, i. 308–418; (2) "Nouvelles recherches sur les lois des proportions chimiques sur les poids atomiques et leurs rapports mutuels," *Mém. Acad. Roy. Belg.*, 1865, 35, 3; *Œuvres complètes*, 1894, i. 419–749.

[5] Gay-Lussac and Humboldt, *Journal de physique*, Paris, 1805, 60, 129.

[6] This had been previously discovered by Cavendish in 1781, and published in 1784.

the ratio of small integers; and this relationship also extends to the volumes of any gaseous substances produced.

Among the examples given by Gay-Lussac[1] were the following:—

One volume of ammonia unites with one volume of muriatic acid (hydrogen chloride), and with either one volume or half a volume of carbonic acid (carbon dioxide) and fluoboric acid (boron trifluoride); nitrous oxide, nitrous gas, and nitric acid (*i.e.* nitrous oxide, nitric oxide, and nitrogen peroxide, to give them their modern names) contain their constituents in the proportions of one volume of nitrogen to half a volume, one and two volumes of oxygen respectively; two volumes of ammonia yield on decomposition three of hydrogen and one of nitrogen; two volumes of carbonic acid result when two of carbonic oxide (carbon monoxide) unite with one of oxygen; and two volumes of steam are produced by the combination of two of hydrogen with one of oxygen.

Unlike the preceding laws, the Law of Combining Volumes is not exact, but only approximately correct. For example, accurate experiments[2] have shown that, at normal temperature and pressure, the ratio of the combining volumes of hydrogen and oxygen is 2·00269 : 1. Further, one volume of nitrous oxide yields 1·00717 volumes of nitrogen (see p. 254). These results are readily understood when the approximate character of the gas laws (see Chap. II.) is taken into consideration. It is probable that under exceedingly small pressures the Law of Combining Volumes is an exact expression of the nature of gaseous reactions (see Chap. IV.).

THE ATOMIC THEORY.

Introduction.—The laws of quantitative composition previously outlined find a ready explanation in the *Atomic Theory*.

The idea that all matter is composed of minute, indivisible particles or atoms is very ancient. The Greek philosophers held this view. Thus, Democritus (born 460 B.C.) referred the differences between substances to variations in the size, shape, position, and motion of the atoms constituting them; while Lucretius, at the end of the first century of the Christian era, expressed views which sound very familiar to those current to-day. A solid he regarded as atoms squeezed closely together; a liquid as similar atoms less closely packed; and a gas consisted of but few atoms with much freedom of motion. These atoms were imperishable, and always in motion; and on the manner in which they combined depended the properties of the substance formed.

Coming down to later times, an atomic theory of matter was very much in vogue in the seventeenth century, and for various phenomena explanations based on the theory were largely sought by Bacon,[3] Boyle,[4] Hooke, and others. Newton went so far as to show, on the assumption of the atomic composition of matter, that Boyle's law for gases must necessarily follow.

The development of quantitative ideas concerning the combination of atoms did not really begin until the close of the eighteenth century, when two Irish chemists, Bryan Higgins (1737–1820), and particularly his pupil and nephew William Higgins (1769–1825), endeavoured to arrive at a knowledge of the number of atoms or ultimate particles which united chemically to form a single ultimate particle of some new compound. Influenced by the principle which Newton had laid down that the particles of any one gas are mutually repellent, both these workers arrived at the view that chemical combination would most readily occur between a single ultimate particle of one substance and a single ultimate particle of a second substance. Thus a single particle of an acid united in all cases with one alkaline particle, and was unable to take up a second, because the first alkaline particle repelled the second and prevented combination. William Higgins, however, recognised combination in multiple proportions, though he held that the union of a single particle of each resulted in the formation of the compound of greatest stability.

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[1] Gay Lussac, *Mém. de la Société d'Arcueil*, 1809, 2, 207; *Alembic Club Reprints* (Clay, 1893), No. 4.

[2] Morley, *Smithsonian Contributions*, 1895, 29, No. 980; *cf.* Scott, *Phil. Trans.*, 1893, 184, 543.

[3] Bacon, *Novum Organum*, 1620.

[4] Boyle, *The Sceptical Chemist* (1661), *The Usefulness of Natural Philosophy* (1663), *The Usefulness of Experimental Knowledge* (1671).

These views are almost precisely similar to those at which John Dalton arrived some years later. The exact origin of Dalton's Atomic Theory has been contested throughout the nineteenth century, but a survey of the evidence renders it almost certain that Dalton had already formulated an atomic theory from the experiments made by him, prior to 1803, on the physical properties of gases, and that the application of this atomic theory to chemical combination was first made when he found, in 1803, that oxygen could be taken up in two different proportions by nitric oxide. Thus the atomic theory preceded the discovery of the Law of Multiple Proportions, and received considerable support from the facts upon which that law was based.[1]

According to the Daltonian theory, an elementary body is regarded as being made up of an enormous number of extremely minute particles, called atoms, alike in kind, and particularly in mass, but differing in each of these respects from the atoms of any other element. In the connected account which Dalton gave in 1808[2] of his atomic theory, he pointed out how important an object it was to be able to arrive at a knowledge of the relative weights of these ultimate particles capable of chemical union, for, having obtained a list of such relative weights, it acted as a guide in investigating the composition of new substances discovered. This application of the theory had, in fact, already enabled him to draw up a table of atomic weights as early as 1803.[3]

Dalton's Atomic Weight System.[4]—The method by which Dalton proceeded to determine atomic weights may now be stated.

The atom was the smallest ultimate particle obtainable of any elementary substance. The atomic weights were the relative weights of these ultimate particles or atoms of the elements.

Since the atomic weights are but relative weights, some one substance must be selected as the standard of comparison. Dalton chose hydrogen, and called its atomic weight unity. The atomic weight of any other element was therefore the ratio of the weight of its atom to the weight of an atom of hydrogen. Its value was arrived at by the analysis of a compound containing the element and either hydrogen itself or some element whose atomic weight had already been fixed by comparison with hydrogen.

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[1] For a detailed account of the development of Dalton's Atomic Theory, see Henry, *Memoirs of John Dalton*, 1854; Roscoe and Harden, *A New View of the Origin of Dalton's Atomic Theory* (Macmillan & Co.), 1896; the papers by A. N. Meldrum on "The Development of the Atomic Theory" (*Mem. Manchester Lit. Phil. Soc.*, 1910, 54, No. 7; 1911, 55, Nos. 3, 4, 5, 6, 19, 22; reprinted in *Chem. News*, 1910 and 1911); also *Avogadro and Dalton*, by A. N. Meldrum (Clay), 1904; *John Dalton*, by J. P. Millington (Dent), 1906.

[2] Dalton, *A New System of Chemical Philosophy*, 2 vols., 1807–10.

[3] Dalton, *Mem. Manchester Lit. Phil. Soc.*, 1805, 1, 271, appendix to paper.

[4] From "A New System of Chemical Philosophy," *loc. cit.*

One most important point had first to be settled. Dalton knew, as expressed in the Law of Multiple Proportions, that two elements might combine in more than one proportion. According to Dalton, the following scheme of chemical combination was possible:—

1 atom of A + 1 atom of B = 1 atom of C, binary,
1 ,, ,, + 2 atoms ,, = 1 ,, D, ternary,
2 atoms ,, + 1 atom ,, = 1 ,, E, ,,
1 atom ,, + 3 atoms ,, = 1 ,, F, quaternary,
etc.

On the basis of the view that like particles repel one another (*cf.* p. 16), Dalton assumed the binary to be the most stable compound. Accordingly, if only one compound of two bodies was known, it was presumed to be binary. If, however, two compounds were known, one was deemed binary and the other ternary (it will be seen that two ternary combinations are possible, with no guiding principle available to select the correct one), etc.

It will be observed that Dalton referred alike to the ultimate particles of elements and of compounds as atoms, distinguishing them as "simple atoms" and "compound atoms" respectively. The preceding rules he applied equally to the combination of elements and of compounds.

Having thus assumed the manner in which substances united, chemical analysis furnished the desired atomic weights. For example, water—at that time the only known compound of hydrogen and oxygen—was assumed to be a binary compound.

Dalton found for the combining ratio hydrogen : oxygen the value 1 : 7; hence these numbers represented the atomic weights of hydrogen and oxygen respectively. Similarly, ammonia was represented by NH, since it was the only compound of nitrogen and hydrogen known, and the atomic weight of nitrogen found to be 5. The atomic weights of compounds were obtained from their combinations by a similar process or else by adding up the atomic weights of their constituent elements.

Early Atomic Weight Systems.—The need of some guiding principle of general application in the determination of atomic weights, such as we now possess in Avogadro's Hypothesis, is most clearly emphasised in the failure of all attempts, prior to 1860, to establish a system of atomic weights generally acceptable to chemists, and before outlining modern methods, a brief account of the three systems in use, in addition to Dalton's, in the first half of the nineteenth century will be given. These are the systems of Berzelius, of Gmelin, and of Gerhardt and Laurent.[1]

Atomic Weight Systems of Berzelius.—Berzelius developed two atomic weight tables; the first, published in 1818,[2] was the outcome of work beginning in 1810; the second, which was far more successful, appeared in 1826.[3]

In developing the first table, Berzelius obtained his results largely from the analyses of oxides, sulphides, and salts. Combination between two substances A and B occurred in such a manner, he considered that an atom of A may combine with 1, 2, 3, or 4 atoms of B. Hence the compositions of the oxides of iron were assumed to be represented by FeO_2 and FeO_3; those of potassium by KO_2 and KO_3. These formulæ were assumed on the ground of simplicity; such formulæ as Fe_2O_3 were rejected.

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[1] Regnault also had a scheme based on Dulong and Petit's Law.

[2] Berzelius, *Lehrbuch der Chemie*, 3 vols., 1808–18. First German edition, 1825–31; 5th edition, 1843–5.

[3] See Berzelius, *Jahresbericht*, 1828, 8, 73.

Berzelius' views on salt formation were very similar to those of Lavoisier. An acid contained oxygen and consisted simply of a non-metal united to that element, no hydrogen being present save in the hydracids HCl, HCN, etc. A salt was formed by the direct union of an acid with a base. Thus, barium sulphate was obtained by direct union of sulphuric acid, SO_3, with baryta, BaO.

Another principle was also used by Berzelius in deriving the atomic weight of oxygen, namely, Gay-Lussac's Law of Volumes. Gay-Lussac came to the conclusion that the weights of equal volumes of gaseous substances were proportional to their combining weights, or as Dalton called them, atomic weights. By comparing the densities of hydrogen and oxygen, therefore, the atomic weight of oxygen could be obtained. Berzelius applied this method, and found the atomic weight to be 16. He also concluded that an atom of water contained 2 atoms of hydrogen and 1 atom of oxygen, because 2 volumes or 2 units by weight of hydrogen combined with 1 volume or 16 units by weight of oxygen.

The assumptions regarding the composition of other substances were less successful, in the light of our present atomic weights; as witness the following numbers he obtained, calculated to the hydrogen standard: $C = 12{\cdot}12$; $O = 16$; $S = 32{\cdot}3$; $Fe = 109{\cdot}1$; $Hg = 406$; $Na = 93{\cdot}5$.

The second system, published by Berzelius in 1826, closely approaches our modern system in the results obtained. It was based on four methods:—

(i.) The composition of oxides. If there exist two oxides of a metal, and the quantities of oxygen, combined with unit weight of metal, are in the ratio 1 : 2, the oxides were MO and MO_2, MO_2 and MO_4, or M_2O_3 and MO_3; if 2 : 3, the formulæ were MO and M_2O_3; if 3 : 4, M_2O_3 and MO_2; if 3 : 5, M_2O_3 and M_2O_5.

(ii.) In salt formation, the amount of oxygen in the electro-negative oxide (the acid) is a multiple of that in the basic oxide. This multiple is also the number of atoms of oxygen present in the acid.

(iii.) Gay-Lussac's Law of Volumes, now applied more extensively than before.

(iv.) Mitscherlich's Law of Isomorphism, according to which the similarity in crystalline form exhibited by two compounds is a consequence of the similar mechanical arrangement in their ultimate particles of equal numbers of "simple atoms" (see Chap. II.).

Berzelius also recognised that Dulong and Petit's Law (see Chap. II.) afforded a method of checking atomic weights, though he himself did not apply it.

Methods (iii.) and (iv.), to which Berzelius owed much of the success of his system, are physical in character. The Law of Volumes was now applied to chlorine and nitrogen, and the knowledge so obtained of the atomic weights of these elements served as a guide in dealing with others.

The application of methods (i.), (ii.), and (iv.) may be illustrated by the following examples, with which Berzelius actually dealt.[1] He found that in normal chromates the amount of oxygen in the acid was three times that in the basic oxide.[1] This showed the chromates to be similar in composition to the normal sulphates. Therefore, if SO_3 represented sulphuric acid, as Berzelius believed, CrO_3 should be the formula for chromic acid.

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[1] Berzelius, *Pogg. Annalen*, 1826, **7**, 397; 1826, **8**, 177.

Next, it was found that the basic oxide of chromium contained only half the amount of oxygen present in the acid oxide, referred to the same amount of metal. Hence (method (i.)), if CrO_3 is the acid oxide, Cr_2O_3 must be the formula for chromic oxide. It will be noticed also that, although Berzelius represented potassium chromate as $KO.CrO_3$, the formula conforms to the principle laid down in method (ii.).

Now, chromic oxide was known to be isomorphous with aluminium and ferric oxides. Hence (method (iv.)), their formulæ must be Al_2O_3 and Fe_2O_3 respectively.

By these methods Berzelius was able to arrive at correct formulæ for a large number of oxides, and hence, also, at approximately correct values, judged by our present-day standards, for atomic weights. His measure of success can be gauged by the following numbers, reduced to the modern standard $O = 16$, from the values given by Berzelius in his 1826 table and based on $O = 100$:—

As = 75·33
Ca = 41·03
C = 12·25
Cl = 35·47

Fe = 54·36
Hg = 202·86
N = 14·18
P = 31·43

S = 32·24
Si = 44·47
Na = 46·62
Ag = 216·61

Only in the cases of the last three elements do the numbers differ fundamentally from modern values.

Gmelin's System of Atomic Weights.—The Berzelian system of atomic weights, however brilliant in conception, came to grief through a principle in which its author placed considerable reliance, namely the application of Gay-Lussac's Law of Volumes. In 1826 Dumas[2] began a series of vapour density determinations, deducing from them atomic weights in the same manner as Berzelius himself. For iodine he found the value 125·5, substantially the same as that of Berzelius; but for mercury he found Hg = 99·45, only about one-half of that obtained, as a result of chemical analysis, by the same investigator. Here, then, by the more extensive use of a method in which Berzelius trusted, was a result obtained at variance with that deduced from chemical analysis. This anomaly was followed by others; a few years later Dumas[3] showed by his physical method that P = 62·2 and S = 93·74, whilst Mitscherlich in 1831[4] added arsenic to the list, with As = 152·6. Avogadro's Hypothesis (*vide infra*, p. 21), which had been put forward as early as 1811, affords a ready explanation of these discrepancies; but that hypothesis was neglected, and these results accordingly discredited in a large measure the system of Berzelius, and paved the way to a readier acceptance of Gmelin's system.

As early as 1820 Gmelin[5] had published a scheme of numbers which he recognised as equivalents or combining weights rather than as atomic weights, but the table of 1843 was an atomic weight table. The principles on which it was founded were similar in character to those of Berzelius. Thus, he recognised the Law of Isomorphism, and, like Berzelius, regarded the strong basic oxides as having formulæ of the type MO. But he refused to recognise the application of the Law of Volumes, relying wholly on combination by weight, as Dalton had done before him, and this in the simplest possible manner. "Let it be granted," he said, "that substances combine in the simplest possible proportions," and "let no atomic weights be admitted smaller than those which actually occur in combination." Therefore he came back to the formula HO for water, and the atomic weights H = 1, O = 8, C = 6, S = 16, etc., as in Dalton's table of 1808.

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[1] This fact is clear from the modern representation of potassium chromate as K_2CrO_4 (*i.e.* $K_2O.CrO_3$).

[2] Dumas, *Ann. Chim. Phys*, 1826, 33, 337.

[3] Dumas, *ibid.*, 1832, 49, 210, 50, 170.

[4] Mitscherlich, *Annalen*, 1834, 12, 137.

[5] Gmelin, *Handbuch der Chemie*, 1817; 2nd edition, 1821; 4th edition, 1843; English translation of latter, 1848-1872.

Atomic Weight System of Gerhardt and Laurent.—While Gmelin's system was gradually coming into use, the foundations of another important scheme were being laid by Gerhardt[1] in a series of papers in 1842–3; his views were adopted and extended by Laurent,[2] who henceforward became his co-worker in the new scheme. Much of the advance which these chemists made came from a study of reactions in organic chemistry. Gerhardt noticed that in equations expressing chemical reactions in which carbon dioxide or water were liberated, two molecules of each of these substances, or multiples of two, always occurred, whereas with ammonia only one was liberated; the system of atomic weights used being that of Gmelin. As the formulæ for carbon dioxide and water on this system were CO_2 and HO respectively, Gerhardt suggested that the equations would be simplified by altering them to C_2O_4 and H_2O_2. Or, as an alternative, simplification could be brought about by doubling the atomic weights of oxygen and carbon, so that the formulæ became CO_2 and H_2O. Similarly, carbonic oxide became CO, and by doubling the atomic weight of sulphur the dioxide became SO_2.

Gerhardt and Laurent now revived Avogadro's hypothesis, or rather Ampère's version of it (see p. 22), and employed it extensively, although they did not go so far as to regard it as of universal application. The reason for their adoption of this hypothesis was that they found the formulæ, CO_2, H_2O, SO_2, and CO, suggested by the above reasoning, were also those which were arrived at on the basis of this hypothesis. They accordingly proposed that the formulæ of all vaporisable substances should be altered where necessary, so that molecules of these substances occupied the same volume in the gaseous state.

The effects of the changes made by Gerhardt and Laurent were far-reaching. The first effect was to require the halving of many of the formulæ in use, necessitating also the halving of various atomic weights, as, for example, that of silver. The formula of silver oxide in turn became Ag_2O; simultaneously Gerhardt and Laurent adopted M_2O and MOH as the formulæ of basic oxides and hydroxides respectively (which led, however, to the employment of atomic weights for various metals only one-half as great as those in use to-day); and Laurent clearly indicated for the first time that a hydroxide was to be considered as a substance intermediate between an oxide and water, thus: M_2O, MOH, H_2O.

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[1] Gerhardt, *J. prakt. Chem.*, 1842, 27, 139; 1843, 30, 1; *Ann. Chim. Phys.*, 1843, (iii.), 7, 129; 1843, 8, 238.

[2] Laurent, *Ann. Chim. Phys.*, 1846, (iii.), 18, 266; and his text-book, *Méthode de chimie*, translated by Odling (Harrison, 1855).

THE MOLECULAR HYPOTHESIS AND THE MODERN SYSTEM OF ATOMIC WEIGHTS.

Avogadro's Hypothesis.—This hypothesis, already referred to in connection with the work of Gerhardt and Laurent, will now be considered in some detail.

The question of the number of ultimate particles or "atoms" in a given volume of gas had exercised the mind of Dalton, who came to the conclusion that in equal volumes of different gases at the same temperature and pressure the numbers of ultimate particles were *not* the same. Gay-Lussac's discovery of the Law of Volumes led him to state that the combining weights of different substances were proportional to their densities. In 1811 Avogadro[1] accepted the accuracy of Gay-Lussac's Law, and pointed out that it was a most natural assumption to conclude that the numbers of "integral molecules" in equal volumes of all gases are the same at the same temperature and pressure. Dalton had also realised this, and, partly for this reason, refused to recognise the accuracy of Gay-Lussac's Law. To Dalton and his contemporaries the smallest particle of a substance that existed in the free state was the atom of the substance, and hence they could not accept Avogadro's hypothesis, which could only be brought into line with facts by assuming that these "atoms" of various elements are capable of subdivision.

Avogadro clearly pointed out the two important consequences which follow from the acceptance of his hypothesis, viz.:—

(i.) *The relative masses of the "integral molecules" of gases are in the ratios of the densities of the gases*

By "integral molecules" Avogadro understood "molecules" as that term is now understood; a precise definition of the term "molecule" is given later (p. 22). In illustration of this deduction, he quoted the densities of oxygen and hydrogen as 1·10359 and 0·07321 respectively (air = 1). The ratio of these numbers, namely, 15·074 : 1, was therefore the ratio of the molecular weights of oxygen and hydrogen.

(ii.) *The "integral molecules" of various gaseous elements are themselves composite.*

Two volumes of hydrogen, it was known, combine with one volume of oxygen, producing two of steam. Since equal volumes of different gases contain equal numbers of "integral molecules," two "integral molecules" of hydrogen must combine with one of oxygen and produce two of steam. Hence this one "integral molecule" of oxygen must undergo subdivision in the process, being halved; or, the "integral molecule" yields two "elementary molecules." The term "elementary molecule" was used by Avogadro with the meaning now attached to the word "atom"

Avogadro thus postulated the existence of two orders of small particles: (i.) **molecules**, which are physical units, being the smallest masses of a substance capable of existence in the free state, and (ii.) **atoms**, the ultimate particles of which elementary bodies are aggregates, which enter into the composition of molecules, and which may or may not be identical with molecules in the cases of the elements. The latter question requires to be determined by experiment; Avogadro's Hypothesis, which serves the primary purpose of determining relative molecular weights, can be utilised for this purpose by applying it to the experimental results such as those summarised in Gay-Lussac's Law of Combining Volumes.

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[1] Avogadro, *Journal de physique*, 1811, 73, 58; *Alembic Club Reprints*, No. 4 (Clay, 1893).

Avogadro's views, unfortunately, received but little notice, and Ampère, who brought forward similar ideas in 1814, met with no better success.

The Modern System of Atomic Weights.—About the middle of last century there came a change in the basis on which the atomic weight system was laid. Dalton's methods were based on weight relationships and chemical analysis; those of Berzelius, partly on chemical analysis, partly on a physical principle (the Law of Isomorphism), and partly on the Law of Volumes, which was insufficient, however, to show him the difference between atom and molecule. Gmelin returned to weight methods. These methods, however, are incapable of solving the problem of the determination of atomic weights. The Law of Combining Weights (*vide supra*, p. 12) becomes, in the language of the Atomic Theory, the statement that elements unite in the ratios of finite multiples of their atomic weights; whence it follows that a simple numerical relationship exists between the atomic weight of an element and each of its combining weights. Farther than this, however, it is not possible to proceed from the Atomic Theory alone.

Gerhardt and Laurent first realised the value of being able, by Avogadro's Hypothesis, to compare matter in its simplest (the gaseous) condition, and so to arrive at correct molecular weights. Cannizzaro's system, in[1] 1858, carried this method to complete success and established our modern system of atomic weights.

In order to realise the full value of Cannizzaro's scheme, it should be borne in mind that four systems of atomic weights were in use by different chemists at the middle of last century—namely, the Berzelian system, a modified form of it, Gmelin's system, and that due to Gerhardt and Laurent. A conference of chemists, called in 1860 at Karlsruhe to discuss the confusion of systems, was made acquainted, at its close, with Cannizzaro's system, which soon became the accepted one.

In brief, Cannizzaro's system made Avogadro's Hypothesis its basis. The molecular weights of substances were first to be found, afterwards the atomic weights of the elements. Applying the hypothesis to the results of the chemical union of gases, Cannizzaro found that the molecule of an element was generally polyatomic; as a rule, diatomic. The anomalies found by Dumas (p. 19) were explained by supposing the molecules of phosphorus, sulphur, and mercury to be tetratomic, hexatomic, and monatomic respectively. Cannizzaro found that his results also accorded with those obtainable on the basis of Dulong and Petit's Law (*vide* p. 89), and he used this law when other methods were not available.

The modern atomic weight system is practically identical with that of Cannizzaro, and rests upon **Avogadro's Hypothesis**, *that equal volumes of all gases, under the same conditions of temperature and pressure, contain equal numbers of molecules.* This is rightly regarded as the basis of the atomic weight system, since it was only by its adoption that the term "atom" acquired its present meaning. *A gaseous molecule is the smallest ultimate particle which can exist in the interior of a mass of pure gas*, and in general **a molecule** may be defined as *that minute portion of a substance which moves about as a whole, so that its parts, if it has any, do not part company during the excursions which the molecule makes;*[2] *its molecular weight* is the weight of this ultimate particle, referred to the weight of the molecule of a standard substance.[1]

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[1] Cannizzaro, *Sunto di un corso di filisofia chimica fatto nella Reale Università di Genova*, 1858 : *Nuovo Cimento*, 1858, vol. vii. ; *Alembic Club Reprints*, No. 18 (Clay, 1911).

[2] See Maxwell, *Theory of Heat* (Longmans & Co.), 1899, chap. xxii.

The fact that oxygen contains (at least) two atoms in its molecule has already been shown, and similar reasoning applies to chlorine, nitrogen, and hydrogen. Thus,

1 volume of hydrogen + 1 volume of chlorine give 2 volumes
of hydrogen chloride,

hence, by Avogadro's Hypothesis, if n is the number of molecules in each volume of gas,

n molecules of hydrogen + n molecules of chlorine give
$2n$ molecules of hydrogen chloride,

or 1 molecule of hydrogen + 1 molecule of chlorine give
2 molecules of hydrogen chloride.

Since each molecule of hydrogen chloride contains, of necessity, hydrogen and chlorine, the molecule of each of these elements must have been halved. The deduction that the molecule of nitrogen is divisible into two parts follows from the fact that two volumes of ammonia when decomposed yield three volumes of hydrogen and one of nitrogen. No chemical or other evidence leads to the conclusion that in these elements there are more than two atoms per molecule (see Chap. VII.).

The **atom** is defined as *the smallest part of an element that is found in any molecule.* Its *atomic weight*, in turn, is defined as *the smallest of the weights of the element contained in the molecular weights of the substances into the composition of which the element enters.*

The determination of atomic weights, in the light of this definition, is dealt with in Chap. VII.

CHEMICAL SYMBOLS AND FORMULÆ. EQUATIONS.

A symbolic chemical notation was used by the alchemists; unlike the modern notation, however, it had only a qualitative meaning. Quantitative chemical notation was originated by Dalton;[2] the system in use at the present time is, in all essentials, that devised by Berzelius.

Each element is denoted by a *symbol*, which is the initial letter of its Latin name. Sometimes a second letter is added when several elements have the same initial letter: *e.g.* carbon, copper (*cuprum*), chlorine, and cæsium are denoted by C, Cu, Cl, and Cs respectively. A full list of symbols is given on p. 25. In order to attach a quantitative significance to these symbols, it might at first sight appear the simplest plan to regard the symbol for an element as standing for *one combining weight* of the element. The *formula* of a compound could then be represented by writing down the symbols of its constituent elements side by side, and its quantitative chemical composition indicated by attaching numerical suffixes to the symbols, in order to denote the relative numbers of combining weights of each element present. A difficulty arises, however, in the compilation of a table of combining weights, since many elements possess more than one combining weight. Accordingly, instead of letting the symbol for an element denote a combining weight, it is chosen to represent *one atom* or *one atomic weight* of the element: *e.g.* the symbols previously given stand for one atom or 12 parts by weight of carbon, one atom or 63·57 parts of copper, one atom or 35·46 parts of chlorine, and one atom or 132·8 parts of cæsium. Further, the formula C_1Cl_4, for example, denotes a compound of carbon and chlorine (carbon tetrachloride), in which for every atom, or 12 parts by weight, of carbon there are four atoms or $4 \times 35{\cdot}46$ parts of chlorine. The affix unity is always omitted, so that the formula is written CCl_4.

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[1] See Chap. IV. for the determination of molecular weights.

[2] Dalton, *A New System of Chemical Philosophy*, 2 vols., 1807–10.

Still retaining this example, it is clear that the formula C_nCl_{4n} would do equally well to denote the composition of the substance, n being any integer. However, it is usual, whenever possible, to write the formula of a compound so that it represents a *molecule*, *i.e.* so that on adding up the weights of all the atoms represented in the formula, the molecular weight of the compound is obtained. Such *molecular formulæ* can only be written for substances of known molecular weight. The molecular weight of carbon tetrachloride having been found to be 153·8, it is clear that the simple formula CCl_4 is also the molecular formula, and denotes that one molecule of the substance contains one atom of carbon and four atoms of chlorine. When the molecular formula of a compound is unknown, it is usual to employ the simplest formula that expresses its composition, this being termed the *empirical formula*, *e.g.* the empirical formula of cupric chloride is $CuCl_2$, but its molecular weight has not been determined.

When the atomic and molecular weights of an element are both known, a molecular formula can be given: *e.g.* the molecular formulæ of oxygen, hydrogen, mercury, and phosphorus, in the gaseous state, are O_2, H_2, Hg, and P_4 respectively.

By means of formulæ, it is possible to express in a very concise manner the results of a chemical change. The formulæ of the reacting substances are written down on the left, and connected together with plus signs to indicate that they have reacted together; on the right, the formulæ of the substances produced are written down, and connected with plus signs to indicate that they are all produced together. A sign of equality between the two groups of formulæ denotes that the substances on the left have been transformed into those on the right, and the necessary numerical coefficients are placed before the various formulæ to make the number of atoms of each element the same on both sides. Such a symbolic representation is termed a *chemical equation*, and was first employed by Lavoisier as a means of expressing chemical reaction. As a simple illustration, the equation

$$2H_2 + O_2 = 2H_2O$$

summarises the following statements: (i.) 2×2 or 4 parts by weight of hydrogen combine with 2×16 or 32 parts of oxygen to produce $2 \times (2 + 16)$ or 36 parts of water; and, since the formulæ are molecular, (ii.) two molecules of hydrogen unite with one molecule of oxygen to produce two molecules of water (steam). In such an equation it is easy to read the relative volumes in which the substances react, by recalling Avogadro's Hypothesis (p. 22) to mind; and the preceding equation is readily seen to express the fact (iii.) that two volumes of hydrogen combine with one volume of oxygen to produce two volumes of steam (all measured at the same temperature and pressure).

As a second example, the equation

$$2KClO_3 = 2KCl + 3O_2$$

expresses the fact that $2(39{\cdot}10 + 35{\cdot}46 + 48)$ or 245·12 parts of potassium chlorate, when decomposed into potassium chloride and oxygen, yield 2{39·10 + 35·46} or 149·12 parts of the former and 6 × 16 or 96 parts of the latter. It is not possible, however, from this equation to make statements corresponding to (ii.) and (iii.) of the previous example, since the formula for potassium chlorate is only empirical.

But whilst a single equation may give a complete quantitative representation of the initial and final condition of reacting substances, it seldom happens that the actual way in which a reaction proceeds can be indicated by it. Thus when potassium chlorate is heated, potassium perchlorate is first formed according to the equation

$$4KClO_3 = 3KClO_4 + KCl,$$

and it is not until a temperature of 395° has been exceeded that oxygen is evolved.[1] We thus see that the reactions may be considerably more complicated than the single equation would lead us to believe.

INTERNATIONAL ATOMIC WEIGHTS, 1917.

		O = 16.			O = 16.
Aluminium	Al	27·1	Molybdenum	Mo	96·0
Antimony	Sb	120·2	Neodymium	Nd	144·3
Argon	A	39·88	Neon	Ne	20·2
Arsenic	As	74·96	Nickel	Ni	58·68
Barium	Ba	137·37	Niton (radium emanation)	Nt	222·4
Bismuth	Bi	208·0	Nitrogen	N	14·01
Boron	B	11·0	Osmium	Os	190·9
Bromine	Br	79·92	Oxygen	O	16·00
Cadmium	Cd	112·40	Palladium	Pd	106·7
Cæsium	Cs	132·81	Phosphorus	P	31·04
Calcium	Ca	40·07	Platinum	Pt	195·2
Carbon	C	12·005	Potassium	K	39·10
Cerium	Ce	140·25	Praseodymium	Pr	140·9
Chlorine	Cl	35·46	Radium	Ra	226·0
Chromium	Cr	52·0	Rhodium	Rh	102·9
Cobalt	Co	58·97	Rubidium	Rb	85·45
Columbium	Cb	93·1	Ruthenium	Ru	101·7
Copper	Cu	63·57	Samarium	Sa	150·4
Dysprosium	Dy	162·5	Scandium	Sc	44·1
Erbium	Er	167·7	Selenium	Se	79·2
Europium	Eu	152·0	Silicon	Si	28·3
Fluorine	F	19·0	Silver	Ag	107·88
Gadolinium	Gd	157·3	Sodium	Na	23·00
Gallium	Ga	69·9	Strontium	Sr	87·63
Germanium	Ge	72·5	Sulphur	S	32·06
Glucinum	Gl	9·1	Tantalum	Ta	181·5
Gold	Au	197·2	Tellurium	Te	127·5
Helium	He	4·00	Terbium	Tb	159·2
Holmium	Ho	163·5	Thallium	Tl	204·0
Hydrogen	H	1·008	Thorium	Th	232·4
Indium	In	114·8	Thulium	Tm	168·5
Iodine	I	126·92	Tin	Sn	118·7
Iridium	Ir	193·1	Titanium	Ti	48·1
Iron	Fe	55·84	Tungsten	W	184·0
Krypton	Kr	82·92	Uranium	U	238·2
Lanthanum	La	139·0	Vanadium	V	51·0
Lead	Pb	207·20	Xenon	Xe	130·2
Lithium	Li	6·94	Ytterbium (Neoytterbium)	Yb	173·5
Lutecium	Lu	175·0	Yttrium	Yt	88·7
Magnesium	Mg	24·32	Zinc	Zn	65·37
Manganese	Mn	54·93	Zirconium	Zr	90·6
Mercury	Hg	200·6			

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[1] Scobai, *Zeitsch. physikal. Chem.*, 1903, 44, 319.

CHAPTER II.

GENERAL PROPERTIES OF ELEMENTS AND COMPOUNDS.

THE PROPERTIES AND LAWS OF GASES.

The Gas Laws.—The experimental laws which describe the behaviour of gases may be enumerated as follows:—

1. *Boyle's Law*, according to which the volume (v) of a given mass of gas is inversely proportional to the pressure (p), provided the temperature remains constant. Mathematically expressed, the law becomes

$$p \propto \frac{1}{v} \text{ or } pv = \text{constant}.$$

2. *The Law of Charles* or *Gay-Lussac*.—This law describes the connection between volume and temperature, by stating that the volume of a gas increases by $\frac{1}{273}$ (or 0·00367) of its value at 0° C. for each centigrade degree rise in temperature, the pressure being assumed to remain constant.

3. The law connecting temperature and pressure at constant volume, according to which each degree rise of temperature on the centigrade scale results in an increase of pressure amounting to 0·00367 of the pressure at 0° C.

4. *Dalton's Law of Partial Pressures*.—This law states that the pressure set up by a mixture of gases is equal to the sum of the pressures exerted in the same space by each of the constituents. (See p. 99.)

5. *Graham's Law of Diffusion of Gases*, according to which the rates at which gases diffuse are inversely proportional to the square roots of their densities (see pp. 33–34).

6. *Gay-Lussac's Law of Combination by Volume*.—This has already been discussed in Chapter I.

The first five laws just mentioned, although established experimentally, find a theoretical basis in the kinetic and molecular theories, from which they can be deduced.[1] Moreover, any of the first three laws can be deduced from the other two.

The Gas Equation.—When speaking of the gas laws, the particular ones generally included under this head are the first three mentioned—namely, those which deal with the alteration of the three factors, temperature, pressure, and volume. A very convenient expression has been adopted, known as the gas equation, which connects together all three laws. It may be deduced n the following way:—

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[1] See O. E. Meyer, *Kinetic Theory of Gases*, translated by Baynes (Longmans & Co., 1899).

Starting with the mathematical expression of the law connecting volume and temperature at constant pressure, namely—

$$v_t = v_0\left(1 + \frac{1}{273}t\right),$$

where v_0 and v_t are the volumes at temperatures 0° and t° respectively, by simple transformation we have—

$$v_t = \frac{v_0}{273}(273 + t),$$

$$v_t = \frac{v_0 \mathrm{T}}{273},$$

where T is the temperature on the absolute scale, and finally—

$$\frac{v_t}{v_0} = \frac{\mathrm{T}}{273}.$$

In brief, this expression states that at constant pressure the volume is proportional to the absolute temperature, or $v \propto \mathrm{T}$.

According to Boyle's law, however, $v \propto \frac{1}{p}$.

If, therefore, the temperature and pressure vary simultaneously,

$$v \propto \frac{\mathrm{T}}{p} \text{ or } pv = \text{constant} \times \mathrm{T} = \mathrm{RT}.$$

If v represents the volume of unit mass, namely, 1 gram, then its value will vary for different gases, and R will likewise vary. By a proper choice of units, however, it is possible to make R the same for every gas to which the equation applies. The chemist usually employs the molecular weight and molecular volume as his units, and the most general form of the gas equation becomes

$$\mathrm{PV} = \mathrm{RT},$$

where P denotes the pressure and V represents the gram-molecular volume, which, according to Avogadro's Hypothesis, is a constant quantity for all gases at the same temperature and pressure. Hence, provided the gram-molecule of a gas is always dealt with, the value of R is independent of the *nature* of the gas, and its numerical value depends only upon the units in terms of which P, V, and T are expressed.

When a substance changes its volume under pressure, work is either done *by* the substance (if it expands) or *on* the substance (if contraction occurs), and so, in accordance with the method employed in measuring work, the product PV represents the work done when one gram-molecular volume of gas is generated under a pressure P. The value of R, measured in work units, *i.e.* ergs, can be obtained as follows:—

At 0° C., or 273° (abs.), and 76 cm. pressure, V = 22,400 c.c. in round numbers. Accordingly P = 76 × 13·59 × 980·6 dynes per square cm., since 13·59 is the density of mercury at this temperature. Hence

$$\mathrm{R} = \frac{\mathrm{PV}}{\mathrm{T}} = \frac{76 \times 13{\cdot}59 \times 980{\cdot}6 \times 22{,}400}{273}$$

$$= 8{\cdot}4 \times 10^7 \text{ ergs.}$$

The equation is sometimes expressed in another way; since mechanical energy and heat energy are quantitatively transformable, $4 \cdot 2 \times 10^7$ ergs being equivalent to 1 gram-calorie of heat (the mechanical equivalent of heat), R can also be expressed in heat units, being obviously approximately equivalent to 2 (more exactly 1·985) calories. Inserting this numerical value of R,

$$PV = 2T.$$

In this form the equation is of particular use in thermo-chemistry, in cases where it is desired to determine heats of reaction between gases. If a reaction be accompanied by expansion or contraction, part of the heat effect observed is due to the work done during the alteration of volume, and this must be allowed for in deducing the actual heat of reaction. At t° C. the production of each gram-molecular volume of gas corresponds to an absorption of $2(273 + t)$ or $546 + 2t$ gram calories owing to the performance of external work.

The Validity of the Gas Laws.—In the foregoing section no question has been raised as to the extent to which the gas laws given are valid. The coefficients of expansion for heat were supposed by Gay-Lussac to be the same for all gases. That this is not so was first definitely proved by Regnault, whose results are given in the following table; a is the coefficient of expansion between 0° and 100°, measured at a constant pressure of one atmosphere.

Gas.	a.	Gas.	a.
Hydrogen . . .	0·003661	Carbon dioxide . .	0 003710
Air . . .	0·003671	Nitrous oxide . .	0·003719
Carbon monoxide . .	0·003669	Sulphur dioxide . .	0·003903

Evidently the value of a departs more and more from that of the true gas (conveniently represented at atmospheric pressure by hydrogen) according to the ease with which the gas can be liquefied. The coefficients of increase of pressure with rise of temperature show the same tendency.

In regard to Boyle's Law, the discoverer's investigations were limited to a range of pressure extending between $\frac{1}{30}$ and 4 atmospheres, and were only able to prove the substantial truth of the relationship. Early in the nineteenth century, Oersted, Despretz, Arago, Dulong, and others turned their attention to the question whether or not Boyle's Law would be valid if pressures considerably greater than atmospheric were applied to a given volume of gas. No trustworthy data were obtainable, however, until the experiments of Regnault, published in 1847,[1] were carried out.

As the result of his experiments, Regnault found that not one of the four gases he employed, namely, hydrogen, nitrogen, air, and carbon dioxide, obeyed Boyle's Law between pressures of 1 and 27 atmospheres, the range used; and further, that whereas hydrogen was less compressible than the law would lead us to expect, the three others were more compressible.

The small range of pressures adopted by Regnault led to inquiries by other investigators, the most important experiments being those of Amagat.[2]

Two series of determinations were carried out. In the first, the pressures employed reached 400 atmospheres and were measured directly, the manometer tube for the purpose being built in the shaft of a coal-mine. In this way the behaviour of nitrogen, hydrogen, oxygen, and air was tested, and, when known, enabled one of these gases, nitrogen, to be used in a manometer instead of a column of mercury. The pressures employed in the second series rose as high as 3000 atmospheres, being measured by a mechanical device in an apparatus based on the principle of the hydraulic press.

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[1] Regnault, "Relation des expériences," 1847; *Mém de l'Acad.*, 1847, **21**, 329.

[2] Amagat, *Ann. Chim. Phys.*, 1880, [v.], **19**, 345; 1881, [v.], **22**, 353; 1883, [v.], **28**, 456, 464; 1893, [vi.], **29**, 68.

In addition to the four gases already mentioned, CO_2, C_2H_4, and CH_4 were also tested. The results both confirmed and very considerably extended Regnault's observations, hydrogen standing alone as a gas less compressible, all the others being more compressible than according to Boyle's Law, when only a comparatively limited range of pressure was employed. When still higher pressures were applied, the value of the product *pv* reached a minimum and thereafter steadily increased, just as with hydrogen.

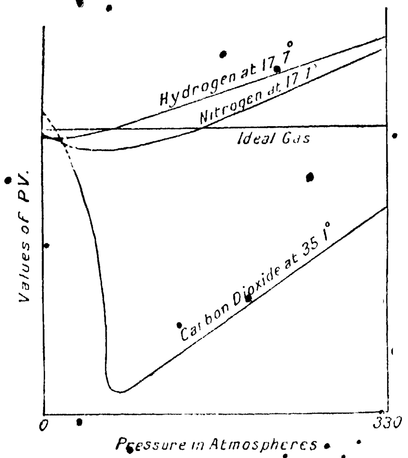

FIG. 1.—Deviations from Boyle's Law.

The most convenient method of representing the facts graphically is to plot, not simply the pressure against volume, but the product *pv* against the pressure *p*, and in the curves (figs. 1 and 2) this method is adopted. Fig. 1 indicates the general types of curves obtained by Amagat, together with that which should be obtained if Boyle's Law were exact—namely, a horizontal straight line. Oxygen and air are similar in behaviour to nitrogen; while the curve for ethylene has a deep minimum point, like that for carbon dioxide. Modern work has shown that the curves for helium and neon resemble that for hydrogen.

Amagat also carried out experiments with carbon dioxide and ethylene at a series of different temperatures, extending from 0° to 258° in the case of carbon dioxide. Fig. 2 represents the results graphically. It will be seen that the minimum point tends to disappear and the gas to behave more as an ideal one the higher the temperature is raised. At ordinary temperatures the hydrogen, helium, and neon curves do not exhibit minima, and it is necessary to cool these gases to a low temperature before curves of this type are obtained.[1]

Boyle's Law, for pressures less than atmospheric, has also been the subject of many investigations,[2] of which the most recent and important are those of Lord Rayleigh.[3] Three ranges of pressure were used—namely, 1–0·5 atmosphere; 150mm.–75mm.; and 1·5mm.–0·01mm. The results obtained between one atmosphere and half an atmosphere pressure are recorded in the follow table, the value of pv referring to 0·5 atmosphere and PV to 1 atmosphere.

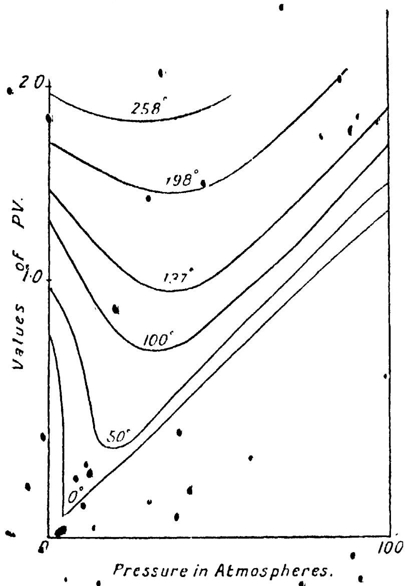

Fig. 2.—Deviation of carbon dioxide from Boyle's Law at different temperatures.

Gas.	Temperature.	$\frac{pv}{PV}$.
H_2	10·7°	0·99974
N_2	14·9°	1·00015
Air	11·4°	1·00073
CO	13·8°	1·00026
O_2. . . .	11·2°	1·00038
N_2O	11·0°	1·00327
NH_3	9·7°	1·00632

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[1] For hydrogen, see Wroblewski, *Monatsh.*, 1888, 9, 1067.

[2] For an account of the investigations on Boyle's Law, both for pressures greater and less than one atmosphere, see Young, *Stoichiometry* (Longmans & Co.), 1908.

[3] Rayleigh, *Phil. Trans.*, 1901, 196, 205; 1902, 198, 417; 1905, 204, 351; *Proc. Roy. Soc.* 1905, 74, 446.

At low pressures, then, just as at high pressures, the gases most readily capable of liquefaction are those which depart to the greatest extent from Boyle's Law, the so-called permanent gases showing little deviation. Over the second range, 150mm.–75mm., the easily liquefiable gases still deviate slightly from the law, whereas the values of pv for nitrogen, air, and hydrogen remain practically constant; but at low pressures, 1·5mm.–0·01mm., all obey Boyle's Law, so far as experiment can determine.

The question of the absolute validity of Boyle's Law under extremely small pressures, however, cannot be decided from the experiments that have been made up to the present time. The error incurred by assuming the validity of Boyle's Law between the two pressures p_1 and p_2 is best expressed by a coefficient $A_{p_1}^{p_2}$ defined by the equation—

$$1 - \frac{p_2 v_2}{p_1 v_1} = A_{p_1}^{p_2}(p_2 - p_1).$$

If Boyle's Law is accurate under extremely small pressures, then when p_1 and p_2 are very close to one another and each is almost nil, the coefficient $A_{p_1}^{p_2}$ should equal zero.[1] Although experiment so far is unable to decide whether this is so or not, it is considered by D. Berthelot, Leduc, and others that such is *not* the case. This conclusion is readily deduced from Van der Waals' equation (*vide infra*), and seems to be in accordance with the experimental evidence; for example, in the case of oxygen the deviation from Boyle's Law is as pronounced at 156 mm. as at 800 mm. pressure.[2]

There is then, in general, at any fixed temperature only one pressure in the immediate neighbourhood of which Boyle's Law is strictly true. This is the pressure at which pv is a minimum.[3]

Van der Waals' Equation.—As it became clear, from the experiments of Regnault and others, that not one of the gas laws held rigidly, a number of investigators sought to obtain an equation which should correctly represent over a wide range the effect of pressure on the volume of a gas. Of these attempts perhaps the most important was that of van der Waals,[4] who introduced two correcting factors into the gas equation.

In order to understand the nature of these corrections, reference must be made to the kinetic theory of gases, on the basis of which the factors were deduced.

The volume of a given mass of gas may be considered as the sum of two quantities, the space occupied by the molecules themselves and that which separates them from one another, the former being small in comparison with the latter when the gas is not strongly compressed. Obviously, the volume available for compression is that of the spaces between the molecules only. Further, according to the kinetic theory, the molecules are considered as being continuously in motion, perfectly elastic, and by their impacts with the sides of the containing vessel, or with any surface exposed to their action, setting up the pressure which is recognised as gas pressure.

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[1] *I.e.* the tangent to the pv-p curve should be horizontal when $p = 0$.

[2] Gray and Burt, *Trans. Chem. Soc.*, 1909, 95, 1633.

[3] Compressibility measurements at pressures below atmospheric are of great utility. As already stated, Avogadro's hypothesis provides a means of finding the molecular weights of substances in the gaseous state. But as the hypothesis requires gases to be compared under the same conditions of temperature and pressure, and since no two gases behave alike towards changes of temperature and pressure, it is obvious that under ordinary conditions the hypothesis cannot be strictly accurate. It is possible, however, by measuring the extent to which different gases deviate from Boyle's Law to introduce corrections for these deviations. The method is explained in Chap. IV. p. 132.

[4] Van der Waals, *Kontinuitat der gasformigen u. flussigen Zustandes*, Leipzig, 1881.

The first correction which must be introduced is due to the size of the molecules, the effect of which will be made clear by the following consideration. If a sphere of 1 cm. diameter start to roll by the shortest possible path from one side of a box to the other, 100 cms. away, it will strike the farther side after moving over 99 cms., whilst a sphere of 2 cms. diameter would need to cover only 98 cms. If, further, the two spheres move backwards and forwards with the same velocity, it is clear that the larger sphere will make the greater number of impacts per second. Hence, the fact that a molecule is of finite size means that the number of impacts made, and therefore the pressure set up, is greater than if it were indefinitely small; and most marked is this difference when the space through which the molecule is required to move before impact is much reduced, as when a gas is subjected to a high pressure. Evidently, then, the actual pressure measured is greater than if the molecules were indefinitely small. Van der Waals found that this increase in pressure was equivalent to a reduction of the volume available for compression in the ratio $\frac{V}{V-b}$, where b is dependent on, although not equal to, the space occupied by the molecules.[1]

The second correcting factor was introduced to allow for the fact that gas molecules are not entirely without influence on one another; for although it is true that at ordinary pressure the attraction may be neglected, at high pressures it is quite appreciable. Joule and Thomson (*vide infra*, p. 42) proved in 1854 that when a highly compressed gas was allowed to expand into a region of low pressure in such a manner that no work was done against external pressure, it nevertheless became slightly colder than before.[2] This phenomenon, which was true for all gases examined except hydrogen (and helium and neon must now be included),[3] is explained by the assumption that at high pressures considerable attraction exists between the molecules of a gas; expenditure of energy is necessary to overcome this attraction when expansion occurs, and consequently a cooling effect is the result. At the centre of a mass of gas, the molecules will be attracted equally in all directions, so that in effect the attractive forces neutralise one another. But near the sides of the containing vessel, the molecules must be on the whole attracted backwards towards the centre of the mass, and for this reason, the velocity with which they strike the sides will be somewhat diminished. The observed pressure is therefore less than would be measured if the molecules were without attractive influence on one another. It was assumed by Van der Waals that the attractive force between two molecules was proportional to the product of their masses—that is, to the square of the density of the gas—or, in turn, to $\frac{1}{V^2}$, where V is the volume. This factor may accordingly be written in the form a/V^2, where a is a constant depending on the nature of the gas. If P represents the observed pressure of a gas whose volume is V, the true pressure—that is to say, the pressure if no attraction occurred—would be $P + a/V^2$.

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[1] As a matter of fact, he calculated that b is equal to *four* times the actual volume occupied by the molecules. Others give the value $4\sqrt{2}$.

[2] This cooling effect is the basis of the modern method of liquefying air, oxygen, etc.

[3] With hydrogen, helium and neon at ordinary temperatures a slight heating effect is produced.

By the introduction of these two factors into the gas equation, the modified form known as van der Waals' Equation is obtained—

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT.$$

This equation expresses the behaviour of a gas over a wide range of temperature and pressure with much greater accuracy than does the ordinary gas equation.

The Diffusion of Gases.—It is a common experience that heavy vapours, such as bromine, can travel upwards and make their presence known, if not by their colour, by their pungent or unpleasant odour. Early experimenters on gases found that a mixture of two gases of different densities do not separate out into layers with the heavy one underneath, and Priestley[1] found that when two gases are carefully brought together with the heavier one underneath, they slowly pass into a homogeneous mixture. Dalton, in 1803,[2] also found that any two of the gases air, nitrogen, hydrogen, oxygen, and carbon dioxide always mix when put into communication by means of tubes.

In 1823 Doberciner observed that hydrogen collected in a flask with a very fine crack escaped into the air, and water rose into the flask, although no hydrogen escaped when the flask was surrounded by a cylinder of the same gas.

The explanation of this phenomenon was furnished in 1832, when, on repeating Doberciner's experiments, Graham found that as hydrogen escaped air entered the vessel. The actual law according to which this diffusion occurred was discovered by Graham in a series of experiments[3] in which tubes, from six to fourteen inches in length, were closed at one end by a thin porous plug of plaster of Paris, filled with gas over water, and diffusion then allowed to proceed. After a given time, the residual gas was analysed in order to determine the amount of the original gas remaining and the amount of air which had entered by diffusion.

Graham found that *the rate of diffusion of a gas is inversely proportional to the square root of its density*. This deduction was based on the following results:—

Gas.	Density. (Air = 1.)	$1/\sqrt{d}$.	Velocity of Diffusion. (Air = 1.)
Hydrogen	0·06949	3·7935	3·83
Methane	0·559	1·3375	1·344
Carbon monoxide	0·9678	1 0165	1·1149
Nitrogen	0·9713	1·0147	1·0143
Ethylene	0·978	1·0112	1·0191
Oxygen	1·1056	0·9510	0·9487
Hydrogen sulphide	1·1912	0·9162	0·95
Nitrous oxide	1 527	0·8092	0 82
Carbon dioxide	1·529	0·8087	0·812
Sulphur dioxide	2·247	0·6671	0·68

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[1] Priestley, *Observations on Air*, 2, 441.

[2] Dalton, *Mem. Manchester Phil. Soc.*, 1805, p. 259.

[3] Graham, *Phil. Mag.*, 1833, 2, 175.

The plaster of Paris plug can be replaced by other porous materials, suc as stucco, but Graham found[1] the best material was a plate of artificia graphite, 0·5 mm. thick. To demonstrate the difference in the diffusiv powers of different gases, use may also be made of thin-walled cells of ur glazed porcelain.

Investigations were also carried out by Graham in which a metal plate pierced by a very fine hole, closed the tube containing the gas. In these experiments the gas was forced through the aperture by a slight excess o pressure in the tube, and its passage outwards under these conditions wa termed *effusion*. For any one gas the rate of effusion was proportional to th difference of pressure on the two sides of the plate, and for different gase under the same pressure conditions the rates were, like the rates of diffusion inversely proportional to the square roots of the densities.

It may be added that the law of diffusion or effusion of gases, experimentally demonstrated by Graham, can be deduced on the basis of the kineti theory of gases.

If a thick porous plug is used, the rate of diffusion is no longer proportional to the square root of the gaseous density, for the friction of a ga with the sides of the pores reduces its velocity. The action is, indeed similar to the passage of a gas through a narrow tube, a process which i called *transpiration*, and which concerns the passage of the gas bodily rathe than with diffusion by molecular movement.

The facts concerning the rate of diffusion of a gas have received practica application in the process called *atmolysis*, whereby the constituents of a gaseous mixture can be partially separated. Thus, if electrolytic gas be passed slowly through a porous clay tube, so much of the hydrogen will escape by diffusion through the walls that the gas collected from the end o the tube will no longer explode. If, instead of electrolytic gas, steam be passed through the tube and heated to a white heat, it is possible to demonstrate that a partial dissociation occurs by the fact that the steam issuing is mixed with an excess of oxygen. Similarly, the products of the dissociation of ammonium chloride may be partially separated, or again, argon can be concentrated in its mixture with nitrogen. As a practical means of purifying gases, however, the process of atmolysis is of little use.

VAPOUR TENSION AND BOILING-POINT OF A LIQUID.

Every liquid exhibits a tendency to evaporate or pass into a state of vapour. If a liquid is sealed in a tube from which air has been removed, evaporation will occur until, for any one temperature, a state of equilibrium is reached between the vapour escaping and that re-entering the liquid. In this condition the pressure which the vapour exerts, called its *vapour pressure*, counterbalances and is therefore equal to the *vapour tension*, or tendency of the liquid to evaporate. The vapour tension and vapour pressure increase with rise of temperature, and in order that the actual value of the vapour tension may be measured liquid must be present as such. Since under these conditions the vapour pressure is a measure of vapour tension, the two terms are often employed indiscriminately.

Two methods are available for the determination of vapour tensions:-

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[1] Graham, *Phil. Trans.*, 1863, 153, 385.

(1) The so-called *statical* method in which the depression of the barometer column caused by evaporating liquid above the mercury is measured.

(2) The *dynamical* method, which consists in causing the liquid to boil under a definite pressure and measuring the boiling-point by immersing a thermometer in the vapour.[1]

On plotting the vapour tension against the temperature, a curve of the general form indicated in fig. 3 is obtained. Its lower limit is normally the melting-point of the solid (or rather the triple-point), but since a liquid can be supercooled, the vapour tension curve can be extended below the melting-point; the upper limit is the critical temperature (*vide infra*, p. 38).

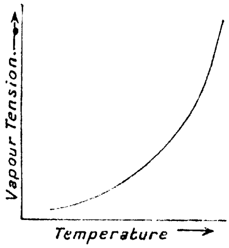

FIG. 3.—General form of vapour tension curve.

The following figures[2] represent the vapour tension (in millimetres mercury) of water at various temperatures.

°C.	mm.	°C.	mm.	°C.	mm.	°C.	mm.
-20	0·960	15	12·728	90	526·00	250	29,951
-10	2·159	20	17·406	100	760·00	300	67,620
0	4·579	25	23·546	120	1,503·00	350	126,924
5	6·528	50	92·17	150	3,578·00	360	141,865
10	9·179	75	289·32	200	11,625·00	364·3	147,904

The above curve is not only the vapour tension curve, but also, as w be evident from the dynamical method of measuring vapour tensions, t curve indicating the relationship between boiling-point and pressure. F the *boiling-point* of a liquid is defined as the highest temperature attainab by a liquid under a given pressure of its own vapour, when heat is appli externally and evaporation occurs freely from the surface. Thus, from t above table, the boiling-point of water at 760 mm. pressure is 100° C., 1503 mm. 120°, and at 92·17 mm., 50°.

Except in special cases, such as in molecular weight determinations, t temperature of the vapour issuing from a boiling liquid and not that of t liquid itself is measured. When the latter is required, two methods, nam those of Beckmann and Buchanan (the latter as used in the Landsberge Sakurai apparatus), are available. In the former process, the source of he is external (usually a gas flame), and superheating and boiling with bumpin are liable to occur. To eliminate superheating, pieces of graphite, porous porcelain or, best of all, platinum tetrahedra are added. Whatever the method of heating, however, a bubble of vapour formed at the bottom of a mass of liquid is under a pressure not only of the vapour, but of the liquid column also, so that when boiling occurs, the temperature at the bottom will be slightly greater than that of the surface layer.[1]

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[1] For the practical details of these methods see, for example, Ostwald and Luther, *Physiko-chemische Messungen* (3rd edition, Leipzig, 1910). The two methods are found to give identical results (see Menzies, *J. Amer. Chem. Soc.*, 1910, 32, 1615).

[2] Landolt-Börnstein, *Physikalisch-chemische Tabellen*, Berlin, 1912.

The boiling-point of a liquid is therefore generally registered by immersing the thermometer, with its bulb surrounded by some material, such as cotton-wool, which has a large surface, in the vapour arising from the freely boiling liquid. A constant temperature is registered when the rate of condensation of vapour on the cotton equals that of evaporation.[2]

Neither air nor any other vapour must be present, for the pressure exerted would then be due in part only to the vapour from the liquid under examination, and too low a boiling-point would be registered.

At high temperatures, boiling-point determinations are effected by measuring, either by platinum resistance thermometers, or by optical pyrometers,[3] the temperatures at which vigorous ebullition of the liquids occurs. In Greenwood's measurements of the boiling-points of metals, the latter were heated, either in a carbon tube crucible or in one of graphite lined with magnesia, by an electrical resistance furnace, and when vigorous ebullition occurred the temperature was noted by an optical pyrometer directed against the bottom of the crucible.

Besides being dependent on the pressure, the boiling-point of a liquid is altered by the presence of a second substance, and hence affords a valuable indication of the purity of the liquid. The nature of this change of boiling-point can be deduced from the discussion of the vapour pressure of mixtures given in Chap. III.

THE BOILING-POINTS OF THE ELEMENTS.

Element.	Boiling-Point.	Pressure.	Authority and Reference.
	°C.	mm.	
Helium	−268·7	760	Onnes, *Proc. K. Akad. Wetensch. Amst.*, 1908, **11**, 168; 1911, **13**, 1093.
Hydrogen	−252·78	760	Travers, Senter, and Jaquerod, *Phil. Trans.*, 1903, **A**, **200**, 105.
Nitrogen	−195·67	760	K. T. Fischer and Alt, *Ann. Physik*, 1903, (4), **9**, 1149.
Krypton	−151·7	760	Ramsay and Travers, *Phil. Trans.*, 1901, **A**, **197**, 47.
Neon	−240 approx.	760	Travers, Senter, and Jaquerod, *loc. cit.*
Fluorine	−187	760	Moissan and Dewar, *Compt. rend.*, 1897, **124**, 1202; 1903, **136**, 785.

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[1] See the Earl of Berkeley and Appleby, *Proc. Roy. Soc.*, 1911, **A**, **85**, 477.

[2] For details of boiling-point measurements, see Ramsay and Young, *Phil. Trans.*, 1884, **175**, 37; Ostwald and Luther, *Physiko-chemische Messungen* (Leipzig, 3rd edition, 1910); also Travers, Senter, and Jaquerod, *Phil. Trans.*, 1903, **A**, **200**, 105; Eumorfopoulus, *Proc. Roy. Soc.*, 1908, **A**, **81**, 339.

[3] See D. Berthelot, *Compt. rend.*, 1895, **120**, 831; 1898, **126**, 410; 1902, **134**, 705 (for Cd and Se); Féry, *Ann. Chim. Phys.*, 1903, [vii.], **28**, 428 (for Zn and Cu); Greenwood, *Proc. Roy. Soc.*, 1909, **A**, **82**, 396; *ibid.*, 1910, **A**, **83**, 483.

THE BOILING-POINTS OF THE ELEMENTS—*continued*.

Elements.	Boiling-Point.	Pressure.	Authority and Reference.
	°C.	mm.	
Argon	−186·1	760	Ramsay and Travers, *loc. cit.*
Oxygen	−182·9	760	Travers, Senter, and Jaquerod, *loc. cit.*
Xenon	−109	760	Ramsay and Travers, *loc. cit.*
Chlorine	− 33·7	760	Johnson and M'Intosh, *J. Amer. Chem. Soc.*, 1909, **31**, 1138.
Bromine	58·7	760	Ramsay and Young, *Trans. Chem. Soc.*, 1886, **49**, 453.
Iodine	181·35	760	,, ,, ,,
Phosphorus	279·3	760	Jolibois, *Thèse*, Paris, 1910; *Compt. rend.*, 1910, **151**, 383.
Mercury	356·7	760	Heycock and Lamplough, *Proc. Chem. Soc.*, 1912, **28**, 3.
Sulphur	444·7	760	Chappuis and Harker, *Phil. Trans.*, 1900, **A**, **194**, 37; Chappuis, *Phil. Mag.*, 1902, (vi.), **3**, 243; Eumorfopoulus, *Proc. Roy. Soc.*, 1908, **A**, **81**, 339; Callendar and Moss, *ibid.*, 1909, **A**, **83**, 106; Waidner and Burgess, *Bureau Stand. Washington*, 1907, **3**, 3, 345.
Arsenic	Sublimes.		
Cæsium	670	760	Ruff and Johannsen, *Ber.*, 1905, **38**, 3601.
Selenium	690	760	D. Berthelot, *Comp. rend.*, 1902, **134**, 705.
Rubidium	696	760	Ruff and Johannsen, *loc. cit.*
Potassium	762 2	760	Heycock and Lamplough, *loc. cit.*
Cadmium	765·9	760	,, ,, ,, ,,
Sodium	882 9	760	,, ,, ,, ,,
Zinc	905·7	760	,, ,, ,, ,,
Magnesium	1120	760	Greenwood, *Proc. Roy. Soc.*, 1909, **A**, **82**, 396; 1910, **A**, **83**, 483.
Thallium	1515	.	Isaac and Tammann, *Zeitsch. anorg. Chem.*, 1907, **55**, 58.
Tellurium	less than 1390	.	Deville and Troost, *Compt. rend.*, 1863, **56**, 891.
Lithium	above 1400	...	Ruff and Johannsen, *loc. cit.*
Bismuth	1420	1 atmos.	Greenwood, *loc. cit.*
Antimony	1440	,,	,, ,,
Lead	1525	,,	,, ,,
Aluminium	1800	,,	,, ,,
Manganese	1900	,,	,, ,,
Silver	1955	,,	,, ,,
Chromium	2200	,,	,, ,,
Tin	2270	,,	,, ,,
Copper	2310	,,	,, ,,
Nickel	2340	30 mm.	Ruff and Keilig, *Zeitsch. anorg. Chem.*, 1914, **88**, 410.
Cobalt	2415	,,	Ruff and Borman, *ibid.*, 1914, **88**, 386.
Iron	2450	1 atmos.	Greenwood, *loc. cit.*; Ruff and Borman, *opus cit.*, p. 259.

The following boiling-points are very uncertain: glucinum (beryllium), >1900; platinum, 2450; rhodium, 2500; ruthenium, 2520; gold, 2530; palladium, 2540; iridium, 2550; molybdenum, 3200; silicon, 3500; boron, 3500; tungsten, 3700.

CRITICAL PHENOMENA.

All gases, when submitted to pressure and cooled sufficiently, are reduced to the liquid state. Of the two factors involved, namely, temperature and pressure, the former is by far the more important, since it is possible to liquefy a gas at ordinary atmospheric pressure by lowering its temperature sufficiently. Thus, at the temperature of boiling hydrogen, all gases except helium pass into either the liquid or the solid state. On the other hand, it is seldom that a pressure as great as 100 atmospheres is required to effect liquefaction. The uselessness of very high pressures is due to the fact that for each gas there is a temperature above which it cannot be liquefied. This temperature is called the *critical temperature* (T_c) of the gas. The pressure necessary to effect liquefaction at this temperature is termed the *critical pressure* (P_c); it is the highest pressure ever required to effect the liquefaction. Few critical pressures exceed 100 atmospheres (see table on p. 131). Before the existence of the critical temperature was known, however, pressures enormously in excess of this were tried, Natterer[1] applying pressures as great as 3600 atmospheres, but without succeeding in liquefying hydrogen, nitrogen, oxygen, and carbon monoxide, even at the temperature of the solid carbon dioxide-ether mixture (p. 39).

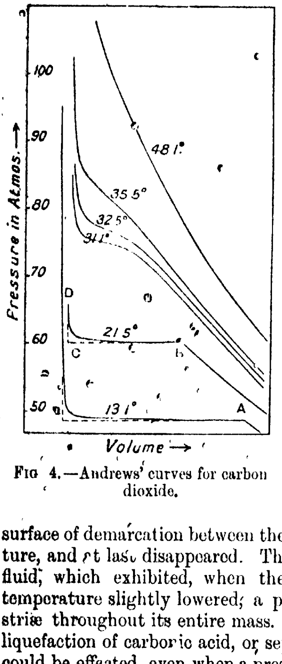

FIG. 4.—Andrews' curves for carbon dioxide.

The existence of the critical temperature was first noticed for ether and a number of other volatile liquids by Cagniard de la Tour in 1822.[2] The significance of his results was not appreciated at the time. Later, Faraday seems to have recognised in the "Cagniard de la Tour Temperature" of a substance the superior limit to its existence in the liquid state; but it was the classic work of Andrews,[3] commenced in 1861, which really led to the discovery of the critical temperature and of the connection between the liquid and gaseous states.

Andrews described his experimental results in the following words: "On partially liquefying carbonic acid (carbon dioxide) by pressure alone, and gradually raising at the same time the temperature to 88° F., or 31·1° C., the surface of demarcation between the liquid and gas became fainter, lost its curvature, and at last disappeared. The space was then occupied by a homogeneous fluid, which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout its entire mass. At temperatures above 88° F. no apparent liquefaction of carbonic acid, or separation into two distinct forms of matter, could be effected, even when a pressure of 300 or 400 atmospheres was applied. Nitrous oxide gave analogous results."[4]

The isothermal curves for carbon dioxide, as determined by Andrews, are shown in fig. 4. Each curve at temperatures below 31·1° C. is made up of three parts, the middle portion being horizontal, and an *abrupt* change of gradient occurs on passing from the horizontal part to the other portions of the isothermal.[1] Their significance may be explained with reference to the isothermal for 21·5° C. The portion AB represents the compression of vapour. (A gaseous substance is called a vapour when its temperature is below its critical temperature.) At B liquefaction commences; the volume diminishes as liquefaction progresses, but the pressure remains constant and equal to the vapour pressure of liquid carbon dioxide at 21·5° C. At C liquefaction is complete, and the portion CD represents the compression of liquid carbon dioxide.

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[1] Natterer, *J. prakt. Chem.*, 1844, **31**, 375; 1845, **35**, 169; 1852, **56**, 127; *Pogg. Annalen*, 1844, **62**, 132; 1855, **94**, 436.

[2] Cagniard de la Tour, *Ann. Chim. Phys.*, 1822, **21**, 127; 1823, **22**, 410.

[3] Andrews, *Phil. Trans.*, 1869, **159** (ii.), 575; 1876, **166** (ii.), 421.

[4] Miller, *Chemical Physics* (Longmans & Co.), 3rd edition (1863), p. 328.

The horizontal portion diminishes with rise of temperature, and at 31·1° C., the critical temperature, it dwindles to nothing, liquid and saturated vapour at the critical pressure having the same specific volume. The isothermals at temperatures above 31·1° C. exhibit no abrupt change of gradient, and no portion of them corresponds with an equilibrium between liquid and vapour; at these temperatures all visible distinction between the liquid and gaseous states has disappeared.

The critical phenomena, so carefully observed by Andrews in the cases of carbon dioxide and nitrous oxide, may be observed with all substances which can be obtained as gases and liquids.

A number of critical constants are given in the table, p. 131.[2]

LIQUEFACTION OF GASES.[3]

The first gas to be reduced to the liquid state was sulphur dioxide, which was liquefied by Monge and Clouet.[4] In 1805–6 Northmore liquefied chlorine, hydrogen chloride, and sulphur dioxide by compression.[5] The first systematic investigation on the liquefaction of gases is due to Faraday,[6] who sealed up the materials necessary to prepare the gas in one limb of a bent tube, cooled the other limb in a freezing mixture of ice and salt, and generated the gas within the closed tube by mixing and warming the materials. Under the combined influence of cold and pressure a number of gases were liquefied, including sulphur dioxide, hydrogen sulphide, euchlorine, cyanogen, ammonia, carbon dioxide, and nitrous oxide. The method was rather dangerous, frequent explosions occurring in the experiments on the last two gases.

Thilorier, in 1834, prepared liquid carbon dioxide on a large scale, using a wrought-iron apparatus and employing Faraday's method of obtaining high pressures.[7] He also solidified carbon dioxide, and discovered that when this solid was mixed with ether, an extremely convenient cooling medium (Thilorier's Mixture) was obtained.

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[1] Andrews did not obtain accurately horizontal parts to his isothermals; the pressure increased slightly as the volume was diminished, and the almost vertical portions of the curves did not start abruptly. This he correctly attributed to the presence of a trace of air in the carbon dioxide.

[2] For methods of determination see Young, *Stoichiometry* (Longmans & Co.), 1908.

[3] See also Hardin, *Rise and Development of the Liquefaction of Gases* (Macmillan & Co.), 1899; Ewing, *The Mechanical Production of Cold* (Camb. Univ. Press), 1908; and Claude, *Liquid Air, Oxygen, and Nitrogen*, translated by Cottrell (Churchill & Co.), 1913.

[4] Fourcroy, *Systèmes des connaissances chimiques*, 1800, vol. ii. p. 74.

[5] Northmore, *Nicholson's Journal*, 1805, **12**, 368; 1806, **13**, 233; *Alembic Club Reprints*, No. 12, p. 69 (Clay, 1896).

[6] Faraday, *Phil. Trans.*, 1823, **113**, 189; *Alembic Club Reprints*, No. 12, p. 10.

[7] Thilorier, *Ann. Chim. Phys.*, 1835, **60**, 427, 432; *Annalen*, 1839, **30**, 122.

Faraday resumed his work on the liquefaction of gases in 1845.[1] He applied pressure by means of two air-pumps, and availed himself of "Thilorier's Mixture" in order to obtain low temperatures. By evaporating this liquid under reduced pressure[2] Faraday reached a temperature of − 110° C., measured by an alcohol thermometer, and succeeded in liquefying ethylene, silicon fluoride, phosphine and boron trifluoride, and solidifying hydrogen bromide, hydrogen iodide, euchlorine, cyanogen, ammonia, sulphur dioxide, hydrogen sulphide, and nitrous oxide. He was unable to liquefy hydrogen, nitrogen, oxygen, nitric oxide, or carbon monoxide, and these gases came to be known as the "permanent gases."

Natterer's unsuccessful attempts to liquefy the "permanent gases" have already been mentioned. Success in this direction was first achieved in 1877, almost simultaneously, by Cailletet in France and Pictet in Switzerland.

Pictet[3] reached a temperature below the critical point for oxygen by judiciously applying the methods that had been previously employed. Liquid sulphur dioxide, boiling under reduced pressure at − 65° C., was used to liquefy carbon dioxide at a pressure of 4 to 6 atmospheres. This liquid in its turn was boiled under reduced pressure, and temperatures varying from − 120° to − 140° C. were thereby obtained. The liquid carbon dioxide cooled the highly compressed oxygen, which condensed to the liquid state. To this "cascade" method of attaining low temperatures, Pictet added the method of continuous cooling; for each of the auxiliary gases, sulphur dioxide and carbon dioxide, underwent a continuous cycle of changes, being liquefied, evaporated under reduced pressure, reliquefied, and so on. The cryogenic laboratories at the Royal Institution, London, and at Leyden, are equipped with low-temperature plant in which the cascade principle is adopted.

Cailletet[4] introduced the method of adiabatic expansion with the performance of external work. The sudden, adiabatic, expansion of a gas against an external pressure causes external work to be performed by the gas, which accordingly suffers a diminution in its internal energy, and falls in temperature. The lowering of temperature obtained in this way may be very great. Cailletet compressed the gas in a capillary glass tube confined over mercury to several hundred atmospheres pressures, cooled the gas to about 0° to − 20° C., and then suddenly released the pressure. In this way he succeeded in liquefying acetylene, nitric oxide, methane, oxygen, carbon monoxide, air, and nitrogen (the first two gases yielded to cold and pressure alone, without any necessity for expansion), and obtained indications of the liquefaction of hydrogen.[5]

The process, as carried out by Cailletet, was of no use commercially, and it was not until 1905 that the method of cooling by adiabatic expansion was successfully worked on a large scale. The method employed consists in dividing a supply of gas, compressed to about 50 atmospheres, into two parts and expanding one suddenly in a cylinder fitted with a piston, thereby performing external work and lowering the temperature of the gas below its critical point. The cold expanded gas is then utilised in cooling the other portion of gas, which liquefies at the pressure employed, and the process is carried on in a continuous manner.[1] The difficulty of lubrication was largely responsible for the failure of previous attempts to carry out this process commercially. The lubricant employed by Claude is petroleum ether, which does not solidify, but only becomes viscous at such low temperatures as - 140° to - 160° C. This procedure for obtaining low temperatures is conveniently combined with the Linde process for liquefying gases, to be described later.

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[1] Faraday, *Phil. Trans.*, 1845, **135**, 155; *Alembic Club Reprints*, No. 12, p. 33.

[2] This method of obtaining low temperatures was first used by Bussy (*Ann. Chim. Phys.*, 1824, **26**, 63).

[3] Pictet, *Compt. rend.*, 1877, **85**, 1214; *Ann. Chim. Phys.*, 1878, (v.), **13**, 145.

[4] Cailletet, *Compt. rend.*, 1877, **85**, 851, 1016, 1213, 1270; *Ann. Chim. Phys.*, 1878, (v.), **15**, 132.

[5] Cailletet, *Compt. rend.*, 1877, **85**, 1270.

Cailletet prepared large quantities of liquid ethylene, which he recommended as a valuable refrigerant, and, employing this liquid, boiling under reduced pressure, as a cooling bath, he succeeded in obtaining liquid methane and oxygen as static liquids.[2] The employment of the same cooling medium by Wroblewski and Olszewski led to the production of liquid oxygen, carbon monoxide, and nitrogen in the static form,[3] and subsequently to the production of considerable quantities of these liquids, and the solidification of nitrogen and carbon monoxide, temperatures as low as - 200° C. being reached. The rapid evaporation of liquid ethylene *in vacuo* leads to a temperature of - 152° C.[4] The utility of liquid ethylene as a refrigerant was also recognised by Dewar,[5] who prepared liquid air and oxygen in large quantities by its aid.

The modern process, by which liquid air, oxygen, etc., may be obtained in large quantities, requires the use of no auxiliary refrigerant; it may be called the method of "self-intensive refrigeration," and was brought forward almost simultaneously by Linde[6] and Hampson[7] in 1895. In this method, the gas to be liquefied is continuously supplied at a high, constant pressure to a long, closely wound, vertical, copper spiral tube, and allowed to expand through a valve attached to the base of the coil. The gas escapes, and passes up at a low, uniform pressure, through the space between the exterior of the coil and its metallic casing. Each portion of gas that expands through the valve undergoes a diminution in temperature, and the cold gas is utilised in lowering the initial temperature of the portion of gas next to be expanded, *i.e.* the cooling effect is intensified, until at length the gas liquefies.

In the ordinary Hampson air-liquefier (fig. 5) the air at A, carefully freed from carbon dioxide and moisture, is delivered into the coil at 150 to 200 atmospheres pressure, and allowed to expand at the nozzle D down to a pressure only a trifle in excess of that of the atmosphere; about [illegible] per cent of the air passing through the apparatus is liquefied, and about a litre and a half of liquid air may be obtained in an hour. The liquid collects in E, and is withdrawn by unscrewing the hollow spindle F G. Owing to the difference in the boiling-points of oxygen and nitrogen, the liquid air is considerably richer in the former element than ordinary atmospheric air.

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[1] Claude, *Compt. rend.*, 1900, **131**, 500; 1902, **134**, 1568; 1905, **141**, 762, 823; see also Mathias, *Revue générale des Sciences*, 15th Sept. 1907.

[2] Cailletet, *Compt. rend.*, 1882, **94**, 1224; 1883, **97**, 1115; 1884, **98**, 1565; 1885, **100**, 1033; *Ann. Chim. Phys.*, 1883, (v.), **29**, 153.

[3] Wroblewski and Olszewski, *Monatsh.*, 1883, **4**, 415; *Compt. rend.*, 1883, **96**, 1140, 1225; *Wied. Annalen*, 1883, **20**, 243.

[4] Wroblewski, *Compt. rend.*, 1883, **97**, 166, 309, 1553, 1884, **98**, 149, 304, 982; **99**, 136; 1885, **100**, 979; 1886, **102**, 1010; *Wied. Annalen*, 1883, **20**, 860; 1885, **25**, 371; **26**, 134; 1886, **29**, 428; Olszewski, *Monatsh.*, 1884, **5**, 124, 127; 1886, **7**, 371; 1887, **8**, 69; *Phil. Mag.*, 1895, (v.), **39**, 188; **40**, 202; and *Compt. rend.*, 1884, **98**, 365, 913; **99**, 133, 184, 706; 1885, **100**, 350, 940; **101**, 238.

[5] Dewar, *Proc. Roy. Inst.*, 1886, p. 550; cf. *ibid.*, 1884, p. 148; *Phil. Mag.*, 1884, (v.), **18**, 210.

[6] Linde, *The Engineer*, 4th Oct. 1895; *Soc. of Arts J.*, 1897, p. 1091; *Eng. Pat.*, 1895, No. 12,528; Linde, *Wied. Annalen*, 1895, (ii.), **57**, 328; *Ber.*, 1899, **32**, 925.

[7] Hampson, *J. Soc. Chem. Ind.*, 1898, **17**, 411; *Eng. Pat.*, 1895, No. 10,165.

The cooling effect produced in the machines of Linde and Hampson is not due to a diminution in the internal energy of the gas caused by its performing external work against the atmospheric pressure, and must therefore be clearly distinguished from that utilised by Cailletet. The fall in temperature is the result of internal work performed in separating the gas molecules farther from one another, thereby overcoming the forces of attraction that operate between them (*vide supra*, p. 32). This thermal effect was first studied by Joule and Thomson.[1] It is quite small, amounting, in the case of air at the ordinary temperature, to only 0·255° C. for a fall in pressure of one atmosphere. It increases, however, as the pressure drop is increased and also as the initial temperature is lowered, and this circumstance was put to practical advantage by Linde and Hampson.

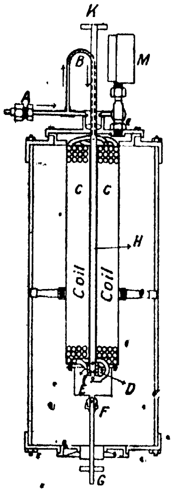

FIG. 5.—Hampson liquefier.

The application of this method to the liquefaction of hydrogen at first sight seems out of the question since a slight rise in temperature occurs with this gas (*vide supra*, p. 29). If, however, the initial temperature of the gas be sufficiently reduced, hydrogen behaves like the other gases, and in 1898 Dewar,[2] by applying the method to hydrogen previously cooled with liquid air, succeeded in obtaining liquid hydrogen. Hydrogen liquefiers have been subsequently described by Travers[3] and Olszewski;[4] the "inversion temperature" of hydrogen, below which it is cooled by free expansion, is $-80·5°$ C.[5]

Helium proved even more difficult to liquefy than hydrogen, but its liquefaction was at length accomplished by Kamerlingh Onnes by the self-intensifying process, after initially cooling the gas to the temperature of liquid hydrogen.[6]

Liquid air and similar volatile liquids are usually collected and preserved in the vacuum flasks introduced by Dewar. These are double-walled glass vessels, the space between the walls being completely evacuated, and the contained liquid thereby vacuum jacketed. The heat conveyed by radiation across the vacuous space to the liquid is only about one-sixth of that which would reach the liquid by conduction and convection in the absence of the vacuum jacket; and this can be diminished to about one-thirtieth part if the interior of the jacket is silvered. The latter procedure, however, is impracticable if for any purpose it is necessary to observe the contents of the flask.

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[1] Joule and Thomson, *Phil Trans.*, 1853, **143**, 357; 1854, **144**, 321; 1862, **152**, 579.
[2] Dewar, *Chem. News*, 1900, **81**, 136.
[3] Travers, *Phil. Mag.*, 1901, (vi.), **1**, 411; *The Study of Gases* (Macmillan & Co., 1901).
[4] Olszewski, *Bull. Acad. Sci. Cracow*, 1902, p. 619; 1903, p. 241.
[5] Olszewski, *Phil Mag.*, 1902, (vi.), **3**, 535; cf. *Bull. Acad. Sci. Cracow*, 1906, 792.
[6] Kamerlingh Onnes, *Compt. rend.*, 1908, **147**, 421; *Proc. K. Akad. Wetensch. Amsterdam*, 1908, **11**, 168; see also *Nature*, 1908, **78**, 370.

PROPERTIES OF SOLIDS.[1]

Melting-Point and its Determination.—The familiar phenomenon of the passage of a crystalline substance from the solid into the liquid state occurs at a definite temperature known as the melting point. More accurately defined, the melting-point is the temperature at which the solid and liquid phases can exist in equilibrium under a given pressure. The effect of pressure in altering the melting-point is very small, as will be seen by the following examples, and further, increase of pressure may bring about either a rise or a fall in the melting-point, according as the substance expands on liquefaction or contracts.

Water (Ice).[2]		Carbon Dioxide.[3]		Phosphorus.[4]	
Melting-Point.	Pressure.	Melting-Point.	Pressure.	Melting-Point.	Pressure.
°C.	Atmos.	°C.	Atmos.	°C.	Atmos.
0	1	-56·7	5·1	44·10	1
- 2·5	336	-47·4	500	45·50	50
- 5	615	-38·0	1000	47·00	100
-10	1155	-20·5	2000	48·45	150
-15	1625	- 4·0	3000	49·85	200
-20	2042	+10·5	4000	52·80	300

The majority of substances have their melting-points raised by an increase of pressure.

Melting-points as usually tabulated indicate the transition temperatures from the solid to the liquid state at atmospheric pressure. The accompanying table records the melting-points of the elements. For salts, the temperatures recorded by various investigators often vary considerably, and no examples are included in the table.[5]

Various processes are available for the determination of melting-points. The first which may be mentioned depends on finding the freezing-point of the liquid, for when certain precautions are taken the freezing-point and melting-point are identical. The precautions are due to the fact that when a liquid is slowly cooled without agitation, or even, in some cases, when slowly and regularly stirred, the temperature falls below the melting-point, or normal freezing-point, and the liquid becomes supercooled. This supercooled condition can be removed by the addition of a trace of the solid phase (a minute amount of ice if the liquid is water) or by the production of the solid phase by agitating the liquid. Both these methods are followed in practice, the latter the more frequently. When crystals once appear in the liquid, freezing rapidly takes place and the temperature, provided the degree of supercooling was only small, rises rapidly to the equilibrium temperature of the solid-liquid mixture, that is, to the melting-point. The Beckmann apparatus is very suitable for the purpose of the determination (see p. 145).

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[1] For distinction between "amorphous" and "crystalline" solids, see p. 47.

[2] Tammann, *Ann. Physik*, 1900, [iv.], 2, 6.

[3] Villard and Jarry, *Compt. rend.*, 1895, 120, 1413; Tammann, *Ann. Physik*, 1899, [iii.], 68, 533.

[4] Hulett, *Zeitsch. physikal. Chem.*, 1899, 28, 666.

[5] See Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, 43, 215; White, *Amer. J. Sci.*, 1909, [iv.], 28, 453 and 474.

Another accurate process consists in surrounding the bulb of a thermometer with the finely divided material in a wide tube and raising the temperature slowly by means of a bath maintained at a point only slightly higher than the contents of the tube, until melting has begun. The mixture of liquid and solid is stirred thoroughly, though not rapidly, the constant temperature registered being the melting-point.

For substances of high melting-point, such as metals, a variety of methods has been adopted:—

1. The substance is heated to its point of fusion in a crucible or porcelain tube, a current of hydrogen or of some inert gas being passed over the surface of the metal, and the temperature noted by inserting the protected ends of a thermo couple;[1]
2. The substance is inserted in the form of a wire into the thermo-element, and its temperature raised until fusion occurs and breaks the circuit;[2] or
3. The metal wire forms part of a circuit and is heated up in a porcelain tube together with the bulb of an air thermometer, the temperature being noted when fusion breaks the electric circuit.[3]

THE MELTING-POINTS OF THE ELEMENTS.

Substance.	Melting-Point.	Authority and Reference.
	°C.	
Helium . . .	below -270	Onnes, *Proc K. Acad. Wetensch. Amsterdam*, 1909, **12**, 175.
Hydrogen . . .	-258·9	Travers, Senter, and Jaquerod, *Phil. Trans.*, 1903, **A**, **200**, 170.
Neon . . .	-253 ?	
Fluorine . . .	-223	Moissan and Dewar, *Compt. rend.*, 1903, **136**, 641.
Oxygen . . .	-218·4	Onnes and Crommelin, *Proc. K. Akad Wetensch. Amsterdam*, 1911, **14**, 163.
,, . . .	-219	Dewar, *Proc. Roy. Soc.*, 1911, **A**, **85**, 589.
Nitrogen . . .	-210·5	K. T. Fischer and Alt, *Ann. Physik*, 1903, [iv.], **9**, 1149; *Sitzungsber. Akad. München*, 1902, p. 209.
Argon . . .	-189·6	Olszewski, *Phil. Trans.*, 1895, **A**, **186**, 253.
Krypton . . .	-169	Ramsay and Travers, *Phil. Trans.*, 1901, **197**, 87.
Xenon . . .	-140	Ramsay and Travers, *loc. cit.*
Chlorine . . .	-102	Olszewski, *Monatsh.*, 1884, **5**, 127.
Niton . . .	- 71	Gray and Ramsay, *Trans. Chem. Soc.*, 1909, **95**, 1073.
Mercury . . .	- 38·85	Vicentini and Omodei, *Atti. Acc. Torino*, 1887, **23**.
Bromine . . .	- 7·3	Van der Plaats, *Rec. Trav. Chim.*, 1886, **5**, 347.

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[1] Holborn and Day, *Ann. Physik*, 1900, [iv.], **2**, 505.

[2] Holborn and Day, *loc. cit.*

[3] Jaquerod and Perrot, *Arch. Sci. phys. nat.*, 1905, [iv.], **20**, 28, 128, 506; for other processes see references given in table to H. von Wartenberg, and G. K. Burgess.

THE MELTING-POINTS OF THE ELEMENTS—*continued.*

Substance.	Melting-Point.	Authority and Reference.
Cæsium	28·25	Rengade, *Bull. Soc. chim.*, 1909, (iv.), **5**, 994.
Gallium	30·15	Lecoq de Boisbaudran, *Compt. rend.*, 1876, **83**, 611.
Rubidium	38·5	Erdmann and Kothner, *Annalen*, 1897, **294**, 55.
Phosphorus	44·1	Hulett, *Zeitsch. physikal. Chem.*, 1899, **28**, 666.
Potassium	62·5	Kurnakow and Puschin, *Zeitsch. anorg. Chem.*, 1902, **30**, 109.
Sodium	97·5	Kurnakow and Puschin, *loc. cit.*
Iodine	114	Lean and Whatmough, *Trans. Chem. Soc.*, 1898, **73**, 156.
Sulphur (rhombic)	112·8	Smith and Carson, *Zeitsch. physikal. Chem.*, 1911, **77**, 661.
,, (monoclinic)	119·25	Smith and Holmes, *Ber.*, 1902, **35**, 2992.
Indium	155	A. Thiel, *Ber.*, 1904, **37**, 175.
Lithium	186	Kahlbaum, *Zeitsch. anorg. Chem.*, 1900, **23**, 220.
Selenium	217	Saunders, *J. Physical Chem.*, 1900, **4**, 423.
Tin	231·9[1]	Waidner and Burgess, *Bureau Stand.*, Washington, 1910, **6**, 149; 1910, **7**, No. 1.
Bismuth	268	Heycock and Neville, *Trans. Chem. Soc.*, 1894, **65**, 65.
Thallium	301	Kurnakow and Puschin, *Zeitsch. anorg. Chem.*, 1902, **30**, 86.
Cadmium	321·0[1]	Waidner and Burgess, *loc. cit.*
Lead	326·9	Holborn and Day, *Ann. Physik*, 1900, (iv.), **2**, 505.
Zinc	419·4[1]	Waidner and Burgess, *loc. cit.*
Tellurium	450	Matthey, *Proc. Roy. Soc.*, 1901, **68**, 161.
Cerium	635	Hirsch, *J. Ind. Eng. Chem.*, 1911, **3**, 880.
Antimony	629·2[1]	Day and Sosman, *Amer. J. Sci.*, 1910, [iv.], **29**, 93.
Magnesium	649	Vogel, *Zeitsch. anorg. Chem.*, 1909, **63**, 169.
Aluminium	658·0	Day and Sosman, *loc. cit.*
Calcium	800	Moissan and Chavanne, *Compt. rend.*, 1905, **140**, 122
Strontium	approx. 800	Guntz and Roederer, *Compt. rend.*, 1906, **142**, 400.
Lanthanum	810	Muthmann and Weiss, *Annalen*, 1904, **331**, 1.
Arsenic (grey)	817°-850° (under pressure)	Jolibois, *Compt. rend.*, 1911, **152**, 1767; 1914, **158**, 184; Goubau, *ibid.*, 1914, **158**, 121.
Neodymium	840	Muthmann and Weiss, *Annalen*, 1904, **331**, 1.
Barium	850	Guntz, *Ann. Chim. Phys.*, 1905, [viii.], **4**, 16.
Germanium	approx. 900	Winkler, *J. prakt. Chem.*, 1886, [ii.], **34**, 177.
Praseodymium	940	Muthmann and Weiss, *loc. cit.*
Silver	960·0[1]	Day and Sosman, *loc. cit.*
Gold	1062·4[1]	,, ,,
Copper	1082·6[1]	,, ,,
Manganese	1260	Burgess and Waltenberg, *J. Washington Acad. Sci.*, 1913, **3**, 371; *Zeitsch. anorg. Chem.*, 1913, **88**, 361.
Glucinum	1280	Fichter and Jablczynski, *Ber.*, 1913, **46**, 1604.
Zirconium	approx. 1300	
Samarium	approx. 1350	
Silicon	1434	Mendenhall and Ingersoll, *Phys. Review*, 1907, **25**, 1.
Nickel	1452·3[1]	Day and Sosman, *loc. cit.*
Cobalt	1478±1·1	Kalmus and Harper, *Canadian Department of Mines*, Report 309, 1914.
Iron	1505	H. C. H. Carpenter, *J. Iron Steel Inst.*, 1908, iii. 290. Burgess and Waltenberg, *loc. cit.*

[1] Temperature on the constant volume nitrogen thermometer scale.

THE MELTING-POINTS OF THE ELEMENTS—*continued.*

Substance.	Melting-Point.	Authority and Reference.
Chromium . .	1520	Burgess and Waltenberg, *loc. cit.*
Palladium . .	1549·2[1]	Day and Sosman, *loc. cit.*
Vanadium . . .	1720	Burgess and Waltenberg, *loc. cit.*
Thorium . . .	greater than 1700	von Wartenberg, *Zeitsch. Elektrochem.*, 1909, **15**, 866.
Platinum . .	1755	Day, *Trans. Faraday Soc.*, 1911, **7**, 136.
Titanium . .	1795	Burgess and Waltenberg, *loc. cit.*
Ruthenium . .	approx. 1900	Mylius and Dietz, *Ber.*, 1898, **31**, 3187. Moissan, *Compt. rend.*, 1906, **142**, 189.
Rhodium . .	1907	Mendenhall and Ingersoll, *loc. cit.*
Columbium . .	1950	von Bolton, *Zeitsch. Elektrochem.*, 1907, **13**, 145.
Osmium . . .	2200–2500	Moissan, *Compt. rend.*, 1906, **142**, 189.
Iridium . . .	2290	Mendenhall and Ingersoll, *loc. cit.*
Boron . . .	Volatilises at temp. of electric arc. 2000–2500	Weintraub, *Chem. News*, 1911, **104**, 157; Tiede and Birnbrauer, *Zeitsch. anorg. Chem.*, 1914, **87**, 129.
Molybdenum . .	2450 ± 30	Pirani and Meyer, *Ber. physik. Ges.*, 1912, **14**, 426.
Tantalum . .	2910	Waidner and Burgess, *J. de physique*, 1907, [iv.], **6**, 830. Pirani and Meyer, *Ber. physik. Ges.*, 1911, **13**, 540.
Tungsten . .	3540 ± 30	Langmuir, *Phys. Review*, 1915, [ii], **6**, 138. See also Waidner and Burgess, *loc. cit.*; Pirani and Meyer, *Ber. physik. Ges.*, 1912, **14**, 426.
Carbon . . .	Volatilises about 3500	Violle, *Compt. rend.*, 1892, **115**, 1273; 1895, **120**, 868.

Vapour Pressure of Solids. Volatilisation and Sublimation.—All solid substances give off vapour, and exert a distinct vapour tension at a fixed temperature. The odour which certain solid substances emit is proof of the existence of a vapour pressure. In certain cases, for example those of the metals, metallic oxides, and salts, the vapour pressure must be exceedingly small at ordinary temperature, but the fact that many metals have been sublimed under low pressures at temperatures far below their melting-points[2] affords evidence of the existence of a perceptible vapour pressure even at ordinary temperatures. Zenghelis[3] has found that a piece of silver foil exposed for some months at the ordinary temperature in a closed vessel containing a metal, or one of its oxides or salts, becomes amalgamated with the metal present in the substance employed.

A solid substance which passes off as vapour without liquefaction is said to volatilise. By cooling the vapours so obtained, condensation to the solid state is again obtained; the whole process of volatilising and condensation is known as sublimation. Thus certain ammonium salts, *e.g.* the chloride, arsenious oxide, and iodine (if heated in a wide vessel), pass off wholly as vapour when heated at atmospheric pressure, and may be purified by the process of sublimation. The explanation of this phenomenon lies in the fact that the melting- and boiling-points lie close together. Increase of pressure, which raises the boiling-point considerably, but has little effect on the melting-point, will increase the range of temperature between the fusion and boiling-points and bring about liquefaction.

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[1] Temperature on the constant volume nitrogen thermometer scale.

[2] Demarçay, *Compt. rend.*, 1882, **95**, 183; Krafft, *Ber.*, 1903, **36**, 1690; 1905, **38**, 262; Krafft and Bergfeld, *ibid.*, 1905, **38**, 254.

[3] Zenghelis, *Zeitsch. physikal. Chem.*, 1905, **50**, 219; 1906, **57**, 90.

The vapour tensions of many solids may be determined from the loss of weight which the substances sustain when a known volume of air or other gas is passed over their surfaces.[1] If the vapour tensions are appreciable, as in the case of ice, it may be measured by the static method used for liquid substances (see p. 35).

The vapour tension curve of a solid substance is of the type shown in fig. 6, the upper limit being the melting-point (or rather, the triple-point). It does not coincide with the curve for the supercooled liquid, but cuts it at a small angle, as was demonstrated on theoretical grounds by J. Thomson[2] and Kirchhoff,[3] and experimentally by Ramsay and Young.[4] A supercooled liquid has a greater vapour tension than the solid at the same temperature.

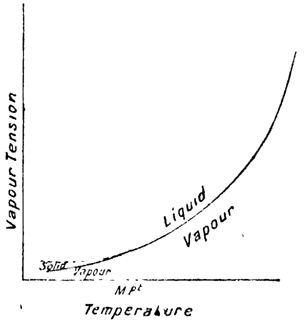

FIG. 6.—Vapour tension curves of solid and liquid.

CRYSTALLOGRAPHY.[5]

Introduction. — Substances which are ordinarily classed as solids may be divided into two groups: those in which the physical properties are the same in all directions; and those in which certain properties, such, for example, as expansion, thermal conduction, and various optical properties, have different values in different directions. Substances belonging to the first group are said to be *amorphous*, those belonging to the second group *crystalline*., Th is considerable evidence for the view that amorphous substances are rea supercooled liquids,[6] in which case every true solid is crystalline. crystalline substance may be defined as one in which certain physical propert differ in different directions radiating from any point within it. This defi tion includes the various *liquid crystals* that have been studied by Lehma and others,[7] but the vast majority of crystalline substances are solids, a these alone will be considered here.

When a body passes from the liquid or gaseous state or from solution the solid state, in favourable circumstances it assumes a definite geometri shape, and is said to *crystallise*. A body formed in this way, bounded plane surfaces or *faces* which intersect in rectilinear *edges* and form so angles or *coigns* where three or more faces intersect at a point, is called a *crystal.*

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[1] See, *e.g.*, Baxter, Hickey, and Holmes, *J. Amer. Chem. Soc.*, 1907, 29, 127, on the vap tension of iodine. Baxter and Grose, *ibid.*, 1915, 37, 1061.

[2] J. Thomson, *Phil. Mag.*, 1874, [iv.], 47, 447.

[3] Kirchhoff, *Pogg. Annalen*, 1858, 103, 206.

[4] Ramsay and Young, *Phil. Trans.*, 1884, 175, 37 and 461.

[5] In the preparation of this section we have been assisted by Mr J. E. Wynfield Rhod B.Sc., whom we take this opportunity of thanking.

[6] See, for example, Tammann, *Schmelzen und Kristallisieren* (Ambrosius Barth, Leip 1903).

[7] Lehmann, *Flüssige Kristalle* (Leipzig, 1904).

It is found that various directions in a crystalline substance are equivalent, *i.e.*, in those directions the physical properties are the same; and equivalent directions are found to be arranged in space in a symmetrical manner. The symmetry of these arrangements is closely connected with the symmetry of the geometrical shapes of crystals, and accordingly the latter are only the outward expression of the internal structures of crystalline substances. The discussion of the physical properties of crystals lies beyond the scope of this work, but a brief account will be given of the *morphology* or form relationships of crystals, and of the connection between the crystalline forms and chemical compositions of substances.[1]

Historical.—The scientific study of crystals dates back merely to the close of the eighteenth century. Among the earlier workers on the subject were Caesalpinus (1600), who observed that the vitriols, sugar, saltpetre, and alum crystallised from solution in characteristic forms, and Hooke,[2] who showed in 1665 how the habits of octahedral crystals of alum could be imitated by building piles of spheres. The laws of the constancy of the angles and cleavage directions were discovered by Steno[3] and Guglielmini[4] but were unfortunately not heeded until the invention of the contact goniometer by Carangeot in 1780 enabled them to be verified experimentally by Romé de l'Isle.[5] The way was thus prepared for the Abbé Réné Just Haüy[6] to show how all the faces of natural crystals are derived from a few simple forms, to state the laws of crystal symmetry, and to apply them to five of the seven now recognised.

Geometrical Crystallography: Fundamental Laws.—The fundamental experimental laws of crystallography are the *Law of the Constancy of Angles*, the *Law of Rational Intercepts*, and the *Laws of Symmetry.* The first of these may be stated in the following manner: under the same physical conditions the angles between corresponding faces on various crystals of the same substance are constant, no matter how much the shapes and appearances of the crystals may vary as a result of unequal development (fig. 7). In other words, the sizes of the faces on a crystal are not important, but only their inclinations to each other. Accordingly, whenever necessary, it is permissible to suppose the faces of a crystal to move parallel to their original positions, in order that *similar faces* (see p. 50) may be equal in size.

The *Law of Rational Intercepts* may be explained in the following manner: Suppose any three edges of a crystal that meet at a point are taken as axes of co-ordinates. Any face of the crystal will intersect one or more of the axes.[1] Choose *one* of them which intersects the *three* axes as the standard, and suppose the intercepts that this plane cuts off from the axes are a, b, and c respectively, measured from the origin. It is only their ratio that matters. Now suppose that *any other face* of the crystal cuts off intercepts in the ratios of $x : y : z$ respectively. They may be expressed in terms of a, b, and c as follows:—

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[1] For further information the reader is referred to the following works: Groth, *Physikalische Krystallographie* (4th edition, Leipzig, 1905); Tutton, *Crystallography and Practical Crystal Measurement* (Macmillan & Co., 1911); Williams, *Elements of Crystallography* (Macmillan & Co., 1892); Lewis, *Treatise on Crystallography* (Cambridge University Press, 1899); Miers, *Mineralogy* (Macmillan & Co., 1902); Baumhauer, *Die neuere Entwickelung der Krystallographie* (Brunswick, 1905); Lubisch, *Physikalische Krystallographie* (Leipzig, 1891); Arzruni, *Physikalische Chemie der Krystalle* (Brunswick, 1893); Fock, *Introduction to Chemical Crystallography*, translated by Pope (Clarendon Press), 1895; Groth, *Introduction to Chemical Crystallography*, translated by Marshall (Gurney & Jackson, 1906); Tutton, *Crystalline Structure and Chemical Composition* (Macmillan & Co., 1910): and Groth, *Chemische Krystallographie*, (Leipzig, 3 vols., 1906–10).

[2] Hooke, *Micrographia*, 1665.

[3] Steno, *De solido intra solidum naturaliter contento* (Florence, 1669).

[4] Guglielmini, *Riflessioni filosofiche dedotte dalle figure de' sali* (Padova, 1706).

[5] Romé de l'Isle, *Crystallographie* (Paris, 1783).

[6] Haüy, *Essai d'une théorie sur la structure des crystaux*, 1784.

$$x : y : z : : \frac{a}{h} : \frac{b}{k} : \frac{c}{l}.$$

It is found that h, k, and l are in the ratios of simple integers, rarely as large as six. This law was first observed by Haüy.

Symmetry.—It is found that crystals may be symmetrical with respect to a point, a line, or a plane.

When to each face on a crystal there corresponds a similar parallel face, the crystal is said to possess a *centre of symmetry*, or to exhibit *centrosymmetry*,[2] *e.g.*, octahedron (fig. 10), cube (fig. 11).

If on rotation about an axis, a crystal presents exactly the same appearance[3] n times in one revolution, the *axis* is said to be one of *n-fold symmetry*. Owing to the operation of the law of rational intercepts (p. 48), *the only values of n are two, three, four*, and *six*, giving rise to *di-*, *tri-*, *tetra-*, and *hexa*-gonal axes of symmetry,[4] and the only angles between pairs of axes of symmetry are 30°, 45°, 60°, and 90°. *An axis of symmetry is always perpendicular to a possible crystal face and parallel to a possible interfacial crystal edge.* As an example, the diagonals of a cube have threefold symmetry.

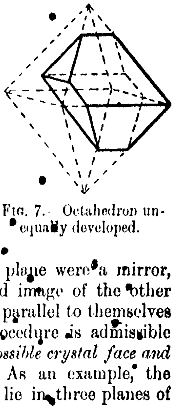

FIG. 7.—Octahedron unequally developed.

A *plane of symmetry* is a plane which divides a crystal into two symmetrical halves, such that if the plane were a mirror, one-half of the crystal would coincide with the reflected image of the other half. It may be necessary to move some of the faces parallel to themselves in order to observe this coincidence, but such a procedure is admissible (p. 48). *A plane of symmetry is always parallel to a possible crystal face and perpendicular to a possible interfacial crystal edge.* As an example, the diagonals of a regular octahedron, taken two at a time, lie in three planes of symmetry which are mutually at right angles.

The preceding *elements of symmetry* may be associated in 31 different ways; accordingly, counting as one class the crystals which possess no symmetry whatever, crystals may be classified according to the types of symmetry they exhibit into 32 classes.[5] Examples are known, corresponding to 31 of these types (see pp. 52-54).[6]

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[1] The face is supposed to be extended, if necessary.

[2] A centre of symmetry is not a true element of symmetry, and centrosymmetry arises from a combination of reflection and rotation (p. 52).

[3] Bearing in mind that only the inclinations, and not the sizes, of the faces are of any consequence.

[4] For simple proofs of this and other important propositions, see H. Marshall, *Proc. Roy. Soc. Edin.*, 1898, **22**, 62.

[5] Hessel, 1830; Gadolin, *Acta Soc. Scient. Fennicæ, Helsingfors*, 1867, **9**, 1.

[6] The properties of crystalline substances are such as to justify the conclusion that the crystalline structure is a homogeneous one, *i.e.* one the parts of which are uniformly

Forms.—Corresponding to any particular face on a crystal, there are certain other faces the presence of which is required by symmetry; the number depends upon the nature of the face and on the grade of symmetry exhibited by the crystal. *A collection of faces, the presence of all of which is required by symmetry, provided one of them be present, is called a form.* A *closed form* is such that its faces, produced, if necessary, completely enclose a space; all other forms are *open forms.* For example, in a crystal which possesses merely a plane of symmetry, the presence of one face necessitates the presence of one other, and the two faces constitute an open form. Clearly such a crystal must be made up of a *combination* of forms, each of two faces. Although the symmetry of a crystal may permit the occurrence of closed forms, it is the exception to find a crystal bounded by faces belonging to only one form; usually a combination of two or more forms is encountered. Only forms corresponding to the same grade of symmetry are found together in combination.

The faces which constitute a form are said to be *similar faces,* and in the succeeding pages it will, for convenience, be assumed that similar faces are equally developed, so that the crystals assume their perfect geometrical forms, free from all distortion.

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repeated throughout. The problem of determining the number of ways in which a homogeneous structure can be built up from its structural units is equivalent to finding the number of ways of arranging homogeneous point systems in space. This can be done in 230 different ways, in each of which the planes of points within the system are related to each other according to the law of rational intercepts; and the symmetry of each of these systems corresponds to that of one or other of the 32 classes of crystals (Bravais, *J. l'École polytechnique, Paris,* 1850, 19, 127; 1851, 20, 102, 197; Sohncke, *Zeitsch. Kryst. Min.,* 1892, 20, 445; Fedorow, *Trans. Russ. Mineral. Soc.,* 1885, 1888, and 1890; *Zeitsch. Kryst. Min.,* 1893, 21, 679; Schonflies, *Krystalsysteme und Krystalstructur,* Leipzig, 1891; Barlow, *Zeitsch. Kryst. Min.,* 1894, 23, 1; 1895, 25, 86; *Sci. Proc. Roy. Dublin Soc.,* 1897, 8, 527; *Brit. Assoc. Report,* 1901, 297; Pope, *Chem. Soc. Ann. Report,* 1908, 5, 258; Hilton, *Mathematical Crystallography* (Clarendon Press, 1903).

The abstract geometrical study of homogeneous assemblages, as perfected by Fedorow, Schönflies, and Barlow, undoubtedly leads to the discovery of all the possible arrangements of the structural units of crystals; but it does not afford any indication of the nature of these units, *i.e.,* whether they are atoms, molecules, or molecular complexes. The remarkable discovery, due to Laue, that a thin slice of a crystal acts as a diffraction grating towards the X-rays and the discovery, by W. L. Bragg, that the X-rays are strongly reflected at crystal faces, have, however, opened up an entirely new field of experimental research which will, in the future, very probably lead to full knowledge both of the nature and disposition of the structural units of a crystal.

An account of the discoveries of Laue and Bragg, and of the researches to which they have led, is beyond the scope of this book. The following references, however, may be of service to the reader: W. Friedrich, P. Knipping, and M. Laue, *Sitzungsber. K. Akad. Wiss. München,* 1912, p. 303; *Ann. Physik,* 1913, [iv.], 41, 971; Laue and Tank, *ibid.,* 1913, [iv.], 41, 1003; Friedrich, *Physikal. Zeitsch.,* 1913, 14, 1079; Wagner, *ibid.,* 1913, 14, 1232; Stark, *ibid.,* 1913, 13, 973; G. Wulff, *ibid.,* 1913, 14, 217; Mandelstam and Rohman, *ibid.,* 1913, 14, 220; Laue, *ibid.,* 1913, 14, 1075; Ewald, *ibid.,* 1913, 14, 465; Wulff and Uspenski, *ibid.,* 1913, 14, 783; Herweg, *ibid.,* 1913, 14, 417; Debye, *Ber. deut. physikal. Ges.,* 1913, 15, 857; Hupka, *ibid.,* 1913, 15, 369; W. L. Bragg, *Nature,* 1912, 90, 410; *Proc. Camb. Phil. Soc.,* 1913, 17, 43; W. H. Bragg, *Nature,* 1912, 90, 572; Barkla and Martyn, *ibid.,* 1912, 90, 435, 647; Moseley and Darwin, *ibid.,* 1912, 90, 594; W. H. and W. L. Bragg, *Proc. Roy. Soc.,* 1913, A, 88, 428; W. H. Bragg, *ibid.,* 1913, A, 89, 246, 248; W. H. and W. L. Bragg, *ibid.,* 1913, A, 89, 277; Moseley and Darwin, *Phil. Mag.,* 1913, [vi.], 26, 210; Barkla and Martyn, *Proc. London Phys. Soc.,* 1913, 25, 206; Terada, *Proc. Tokyo Math. Phys. Soc.,* 1913, 7, 60; M. de Broglie, *Compt. rend.,* 1913, 156, 1153; M. de Broglie and Lindemann, *ibid.,* 1913, 156, 1461; also the following reviews: Bragg, *Science Progress,* 1913, 7, 372; Barker, *Ann. Report Chem. Soc.,* 1913, 10, 233; Kaye, *X-Rays* (Longmans & Co., 1914).

Crystallographic Notation.—In order to express briefly the various crystal forms, a symbolic method is employed, based upon the principles of co-ordinate geometry. A point within the crystal is taken as the origin of co-ordinates, and three *crystallographic axes* of co-ordinates chosen, parallel to three crystal edges not lying in the same plane or parallel to one another. Taken two by two, these axes lie in three *axial planes*, dividing space into eight octants. Whenever possible, axes of symmetry are for simplicity chosen as co-ordinate axes, since they are always parallel to possible crystal edges; preferably, the axes of more than twofold symmetry are selected.

A face that lies in the octant XOYZ (fig. 8), and cuts each of the axes, is chosen as the *fundamental face* or *parametral plane*, and the ratios of its intercepts on the axes are taken as the ratios of the units of length, in terms of which measurements along the three axes are expressed. Hence, in general, measurements are made in three different scales, one for each axis. The axes are conventionally drawn, as shown in fig. 8, and the intercepts or *parameters* a, b, and c of the fundamental face are always referred to in a standard order: firstly, a on the front to back axis; secondly, b on the left to right axis; and thirdly, c on the vertical axis. The ratios of the parameters or *axial ratios* $a : b : c$, together with the angles $YOZ = \alpha$, $ZOX = \beta$, $XOY = \gamma$, constitute the *crystallographic constants* of a crystal. The value of b is generally put equal to unity.

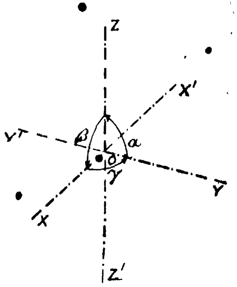

FIG. 8.—Crystallographic axes.

From what has been already stated (p. 49), it is seen that the intercepts x, y, and z of any other face of a crystal are related to the axial ratios $a : b : c$ as follows:—

$$x : y : z :: \frac{a}{h} : \frac{b}{k} : \frac{c}{l},$$

where h, k, and l are in the ratios of simple integers. The face is therefore given the *symbol* (hkl), and h, k, l (expressed in their lowest terms) are called the *indices* of the face.[1] It will be noticed that they are inversely proportional to the intercepts of the face. As an example, the symbol (112) means that the crystal face cuts off intercepts on the axes the *lengths* of which are in the ratios of $\frac{1}{1} : \frac{1}{1} : \frac{1}{2}$, *i.e.* 2 : 2 : 1, the scales of measurement along the axes being in the ratios of $a : b : c$; hence the *absolute* lengths of the intercepts are in the ratios of $2a : 2b : c$. Whenever *zero* occurs as an index, it means that the corresponding intercept is infinitely great, *i.e.* that the plane is parallel to the axis.

To indicate that intercepts are measured along OX′, OY′, OZ′ (fig. 8) the corresponding indices are written *with minus signs above them.* When the symbol of a face is enclosed in brackets, *e.g.* $\{hkl\}$, it stands for *all the faces belonging to the form of which* (hkl) *is one face.* Usually the symbols for the various faces of a form only differ in the order of taking the same indices and in the signs attached to them, *e.g.*, the eight faces of the octahedron (p. 57) are (111), $(1\bar{1}1)$, $(\bar{1}11)$, $(\bar{1}\bar{1}1)$, $(11\bar{1})$, (111), (111), and $(\bar{1}\bar{1}\bar{1})$.

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[1] This index system of notation, now almost universally employed, is due to Miller (Miller, *Treatise on Crystallography* (Cambridge University Press, 1839)).

Crystal forms are named as follows: *pyramids* $\{hkl\}$, each face of which cuts all three axes; *prisms* $\{hk0\}$, each face of which cuts the lateral axes and is parallel to the vertical axis; *domes* $\{h0l\}$ or $\{0kl\}$, each face of which cuts the vertical and one lateral axis, but is parallel to the other; and *pinacoids* $\{h00\}$, $\{0k0\}$, or $\{00l\}$, in which each face cuts one axis and is parallel to the other two. The symbol for the fundamental (pyramid) face is obviously (111).

Crystallographic Classes.—It has been already mentioned (p. 49) that, according to the elements of symmetry they possess, crystals may be classified into **32 classes**. These classes are as follows:—

TRICLINIC SYSTEM.

1. *Asymmetric.* — No elements of symmetry. The faces are simply arranged in accordance with the law of indices; *e.g.* calcium thiosulphate, $CaS_2O_3.6H_2O$.

2. *Holohedral.* — A centre of symmetry only[1]; *e.g.* copper sulphate, $CuSO_4.5H_2O$.

MONOCLINIC SYSTEM.

3. *Domal.*—A plane of symmetry only; *e.g.* potassium tetrathionate, $K_2S_4O_6$.

4. *Sphenoidal.*—One digonal axis of symmetry only; *e.g.* tartaric acid.

5. *Holohedral.*—One digonal axis, perpendicular to a plane of symmetry; *e.g.* potassium magnesium sulphate, $K_2SO_4.MgSO_4.6H_2O$.

ORTHORHOMBIC SYSTEM.

6. *Bisphenoidal.* — Three mutually perpendicular digonal axes of symmetry; *e.g.* magnesium sulphate, $MgSO_4.7H_2O$.

7. *Pyramidal.* — One digonal axis and 2 mutually perpendicular planes of symmetry parallel to it; *e.g.* magnesium ammonium phosphate $Mg(NH_4)PO_4.6H_2O$.

8. *Holohedral.*—Three mutually perpendicular digonal axes, and 3 planes of symmetry, each of which contains two of the digonal axes; *e.g.* potassium sulphate, K_2SO_4.

TETRAGONAL SYSTEM.

9. *Pyramidal.*—One fourfold axis of symmetry; *e.g.* lead molybdate, $PbMoO_4$.

10. *Bisphenoidal.*—One fourfold axis and a plane of compound symmetry perpendicular to it (*i.e.* a centre of symmetry); *e.g.* $2CaO.Al_2O_3.SiO_2$.

11. *Trapezohedral.*—One fourfold axis and 4 twofold axes perpendicular to the first-named and separated by 45° from one another; *e.g.* strychnine sulphate.

12. *Bipyramidal.*—One fourfold axis and a plane of symmetry perpendicular to it; *e.g.* calcium tungstate, $CaWO_4$.

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[1] *I.e.* symmetry that results from reflection in a plane (plane of compound symmetry) and subsequent rotation through 180°.

13. *Ditetragonal bipyramidal.*—One fourfold axis in which intersect 4 planes of symmetry, separated from one another by 45°; *e.g.* iodosuccinimide.

14. *Scalenohedral.*—One fourfold axis and a plane of compound symmetry perpendicular to it; 2 mutually rectangular twofold axes in the latter plane and 2 symmetry planes intersecting in the fourfold axis and bisecting the angles between the twofold axes; *e.g.* potassium dihydrogen phosphate, KH_2PO_4.

15. *Holohedral.*—The 5 axes of (11), the 4 symmetry planes of (13), and the 1 plane of (12); *e.g.* zircon, $ZrSiO_4$.

TRIGONAL SYSTEM.

16. *Pyramidal.* — One threefold axis only; *e.g.* sodium periodate, $NaIO_4.3H_2O$.

17. *Rhombohedral.*—One threefold axis and a "centre of symmetry"; *e.g.* dioptase, CuH_2SiO_4.

18. *Trapezohedral.*—One threefold axis and 3 twofold axes perpendicular to it and separated from one another by 60°; *e.g.* quartz, SiO_2.

19. *Bipyramidal.*—One threefold axis and a plane of symmetry perpendicular to it; no example known.

20. *Ditrigonal pyramidal.*—One threefold axis in which intersect 3 symmetry planes separated from one another by 60°; *e.g.* tourmaline.

21. *Ditrigonal scalenohedral.*—As in 20, but, in addition, 3 twofold axes in a plane perpendicular to the threefold axes, these axes bisecting the angles between the symmetry planes; *e.g.* calcite, $CaCO_3$.

22. *Holohedral.*—As in 21, but, in addition, a plane of symmetry perpendicular to the threefold axis; *e.g.* benitoite, $BaTiSi_3O_9$

HEXAGONAL SYSTEM.

23. *Pyramidal.* — One sixfold axis only; *e.g.* strontium antimonyl tartrate.

24. *Trapezohedral.*—One sixfold axis and 6 twofold axes in a plane at right angles to the first, the latter axes being separated from one another by 30°; *e.g.* the double salt formed by barium antimonyl tartrate and potassium nitrate.

25. *Bipyramidal.*—One sixfold axis and a plane of symmetry perpendicular to it; *e.g.* apatite, $Ca_5F(PO_4)_3$.

26. *Dihexagonal pyramidal.* — One sixfold axis in which intersect 6 symmetry planes separated from one another by 30°; *e.g.* cadmium sulphide, CdS.

27. *Holohedral.*—One sixfold axis; 6 symmetry planes as in (26); 1 symmetry plane as in (25); and 6 twofold axes as in (24), the latter being the intersections of the six symmetry planes with the seventh symmetry plane (*i.e.* the one perpendicular to the sixfold axis); *e.g.* beryl.

CUBIC SYSTEM.

28. *Tetrahedral pentagonal dodecahedral.*—Three mutually rectangular twofold axes parallel to the edges of, and 4 threefold axes parallel to the diagonals of a cube; *e.g.* barium nitrate, $Ba(NO_3)_2$.

29. *Pentagonal-icositetrahedral.* — Three mutually rectangular fourfold

axes, parallel to the edges of, and 4 threefold axes parallel to the diagonals of, a cube. Also 6 twofold axes perpendicular to the faces of the rhombic dodecahedron (see p. 57); *e.g.* cuprite, Cu_2O.

30. *Dyakis-dodecahedral.*—Axes as in (28); and 3 planes of symmetry, each perpendicular to a twofold axis; *e.g.* iron pyrites, FeS_2.

31. *Hexakis-tetrahedral.*—Axes as in (28), and 6 planes of symmetry which may be regarded as bisecting the angles between the planes mentioned in (30); *e.g.* tetrahedrite, Cu_3SbS_3.

32. *Holohedral.*—Axes as in (29), 3 symmetry planes as in (30), and 6 more as in (31); *e.g.* fluorspar, CaF_2.

In addition to those given in the preceding tabular outline, numerous other class-names are in use, the meanings of which will be apparent from the following definitions:—

A *di-n-gonal* axis is one that is the intersection of n planes of symmetry.

Holoaxial symmetry is present when an n-gonal axis is associated with digonal axes perpendicular to it but with no planes of symmetry.

Equatorial symmetry is produced when an n-gonal axis is perpendicular to a plane of symmetry (equatorial plane).

Polar symmetry is produced when an n-gonal axis is perpendicular to no plane and no axis of even symmetry.[1]

Alternating symmetry is that which arises by reflection across an equatorial "plane of compound symmetry" (p. 52), followed by rotation about the axis perpendicular to that plane.

Crystallographic Systems and Axes.—The preceding 32 *classes* are for convenience grouped into **7 systems**, as indicated above, according to the nature of the crystallographic axes to which they are referred and the parameters of the fundamental pyramidal faces. It has been stated (p. 51) that the crystallographic axes must be chosen parallel to crystal edges, and that they are usually chosen parallel to axes of symmetry. The manner in which this is done will now be explained.

1. *Triclinic system.*—There being no axes of symmetry, the crystallographic axes are chosen parallel to three crystal edges. From the symmetry of the system, no axial angle can equal 90°, and no two intercepts of any face can be equal. Hence a *triclinic crystal* is said to be referred to *three oblique and unequal axes*, and in describing such a crystal the angles a, β, and γ must be stated and also values of a and c of the axial ratios $a : 1 : c$. One axis is arbitrarily chosen as vertical axis. It usually corresponds to a direction in which the crystal is well developed. Of the other two axes, the longer or *macro*-axis is placed from left to right, and the shorter or *brachy*-axis from front to back.

2. *Monoclinic system.*—In the holohedral class (class 5) the axis of symmetry is taken as the left to right crystallographic axis or *ortho*-axis: for the vertical axis and front to back or *clino*-axis two directions in the plane of symmetry are selected that are parallel to crystal edges. A similar arrangement of axes is clearly possible for class 3 (p. 52), since the plane of symmetry is perpendicular to a possible crystal edge, and also for class 4 (p. 52), since the digonal axis is perpendicular to a possible crystal face.

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[1] The arrangement of faces around one end of a polar axis is independent of the arrangement about the other end, and a crystal with a polar axis is said to be *hemimorphous*. Such crystals exhibit the phenomenon of pyroelectricity; *e.g.* tourmaline.

From the symmetry of each class in this system it follows that no crystal face can have two equal intercepts on the axes. Hence, in describing a monoclinic crystal the values of a and c in the axial ratios $a : 1 : c$ must be stated and also the magnitude of the angle β. Obviously both α and γ are equal to 90°. *Monoclinic crystals* are therefore said to be referred to *three unequal axes, two of which are perpendicular to the third but not at right angles to each other.*

3. *Orthorhombic system.*—In the holohedral class (class 8) the three digonal axes are chosen as crystallographic axes. The same choice is made in class 6 (p. 52). In class 7 the digonal axis forms one crystallographic axis, and the intersections of the symmetry planes with a plane perpendicular to the digonal axis form the other two, since they are parallel to possible crystal edges (p. 49). Thus in each case the three axes of reference are mutually perpendicular; but in no case is it possible for any crystal face to have two equal intercepts. Hence in specifying an *orthorhombic crystal* it is necessary to state the values of a and b in the axial ratios $a : 1 : c$; and such a crystal is said to be *referred to three mutually perpendicular but unequal axes.* The vertical, *macro-*, and *brachy-*axes are chosen as described for monoclinic crystals.

4. *Tetragonal system.*—Each class in this system is characterised by a fourfold axis of symmetry, which is chosen for the vertical crystallographic axis. The other two axes of reference are chosen perpendicular to the vertical axis and to one another.[1]

In classes 11, 14, and 15 (pp. 52 and 53) these lateral axes are chosen parallel to diad-axes of symmetry. In each class of this system a crystal face cutting off equal intercepts on the lateral axes is possible, but a lateral intercept can never equal a vertical intercept. Hence, the axial ratios $a : 1 : c$ become $1 : 1 : c$, and it is only necessary to state the value of c when describing a tetragonal crystal. A *tetragonal crystal* is therefore referred to *three mutually perpendicular axes, two of which are equal to one another but not to the third.*

5. *Trigonal system.*—Each class in this system is characterised by a trigonal axis of symmetry. The best method of choosing the crystallographic axes (Miller's method) is one in which axes of symmetry are not employed, but, instead, three axes are chosen, symmetrically arranged about the trigonal axis, parallel to three possible crystal edges and not lying in one plane. It is possible, however, to choose the axes of reference as in the case of the hexagonal system, and since this method (the Bravais-Miller system) is perhaps the simpler to follow, the former will not be discussed here.

6. *Hexagonal system.*—Each of the five classes included in this system is characterised by an axis of sixfold symmetry, which is chosen as the vertical crystallographic axis. Instead, however, of choosing two more axes of reference, three more are selected, arranged symmetrically about the vertical axis in a plane perpendicular to it. Their positive directions are regarded as being separated by 120°, as shown in fig. 9.[2] The symbol of a face, therefore, contains four indices, which cannot, however, be all independent

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[1] These represent directions parallel to possible crystal edges (see p. 49).

[2] A little consideration of the propositions on p. 49 and the nature of a hexagonal axis will suffice to show that such axes may be selected in conformity with the requirement that they shall be parallel to possible crystal edges.

of one another. In fact, any lateral index can be calculated from the other two lateral indices, since the sum of the lateral indices is zero. The four indices are always cited in the order x, y, z, w of fig. 9.

The simplest pyramidal face in any class belonging to this system intercepts a on the x axis, is parallel to the y axis, intercepts $\bar{a}$ on the z axis and c on the w axis. Hence its symbol is $(10\bar{1}1)$. Each of the other faces of this form likewise cuts off intercepts numerically equal to a on the lateral axes and c on the vertical axis, c never being equal to a. *Hexagonal crystals* are therefore said to be referred to *three equal lateral axes inclined to one another at* 120°, *and a vertical axis, perpendicular but not equal to the lateral axes.* The ratio c/a is called the axial ratio, and must be given when describing a hexagonal crystal.

7. *Cubic system.*—Each of the five classes belonging to this system is characterised by four trigonal axes of symmetry parallel to the diagonals of a cube, the three mutually rectangular edges of which are taken as the directions of the crystallographic axes. In classes 28, 30, 31 (pp. 53-54) the crystallographic axes are axes of twofold symmetry; in classes 29 and 32 they are axes of fourfold symmetry. In each class, the plane which cuts off equal intercepts on all three axes of reference is a possible crystal face. Hence *cubic crystals* are said to be referred to *three equal and mutually rectangular axes.* The axial ratios $a : 1 : c$, then, are always equal to $1 : 1 : 1$, and so need not be mentioned.[1]

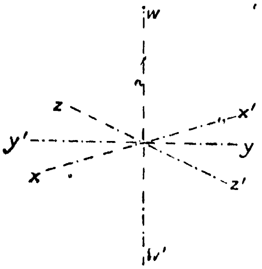

FIG. 9.—Hexagonal crystallographic axes.

Hemihedrism. Enantiomorphous Forms.

—In order to describe a crystal completely it is necessary to state not only its class, the system to which it belongs, and the axial ratios when necessary, but also to state the various *forms* (p. 50) present. An account should therefore be given of the forms belonging to each crystal class; it is, however, beyond the scope of this book. It will be noticed that in each system the class exhibiting the highest grade of symmetry has been called the *holohedral* class. In the following seven sections the holohedral forms will be described, and in addition a few forms belonging to classes of lower symmetry will be included. A few general remarks upon the classes of lower symmetry may, however, be made at this point.

In the first place, certain forms belonging to classes of lower symmetry are geometrically indistinguishable from the holohedral forms, although crystallographically they must be regarded as different.[1] Others may be conveniently regarded as derived from holohedral forms by the symmetrical disappearance of one-half of the faces, and, in accordance with this old-fashioned method of deriving them, are called *hemihedral* forms. A holohedral form gives rise in this way to two hemihedral forms, termed *positive* and *negative* respectively; and they must be regarded as two distinct forms, although when their method of derivation is lost sight of the two forms may be geometrically indistinguishable.[2] In certain cases, however, the + and − forms are not geometrically identical, but are enantiomorphous, *i.e.* one is the mirror-image of the other. Such forms are known as *enantiomorphous forms*, and the crystals which exhibit them are often optically active.[3]

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[1] It will be noticed that with substances that crystallise in the systems of lower symmetry the choice of crystallographic axes is to a certain extent arbitrary. The "setting" of a crystal is said to have been effected in different ways when two observers have chosen different sets of axes in describing it. It has, however, been pointed out by Fedorow that, from the points of view of crystal structure and chemical crystallography, there can only be one correct setting for any crystal—namely, that in which the parametral ratios are measures of the dimensions of the "space-lattice" framework upon which it is built. Further, Fedorow has shown how the correct setting may be deduced (Fedorow, *Zeitsch. Kryst. Min.*, 1904, 38, 321; 1909, 46, 245; 1911, 48, 400; Sokolow and Artemiew, *ibid.*, 1911, 48, 377; Barker, *Ann. Report Chem. Soc.*, 1913, 10, 238).

In addition to hemihedral forms, there are also *tetartohedral* and *ogdohedral* forms, derived by the suppression of three-fourths and seven-eighths of the faces of holohedral forms respectively.

Cubic System (*Regular*, *Isometric or Tesseral*).—*Holohedral* class (32 on p. 54). There are 7 simple forms, all closed (figs. 10 to 17 respectively); forms i., ii., and iii. are fixed forms, iv. to vii. are variable forms:—

(i.) The *octahedron*, {111}, composed of 8 pyramid faces; *e.g.* spinel, $MgO.Al_2O_3$, arsenious oxide, As_4O_6.

(ii.) The *cube*, {001}, composed of 6 pinacoid faces; *e.g.* sodium chloride, $NaCl$, fluorspar, CaF_2.

(iii.) The *rhombic dodecahedron*, {110}, composed of 12 prism faces; *e.g.* garnet, $R^{II.}{}_3.R^{III.}{}_2(SiO_4)_3$.

(iv.) The *tetrakis-hexahedron*, {*hk*0}, or four-faced cube, with 24 prism faces; *e.g.* copper {210}, and fluorspar as {310} in combination with {001}.

(v.) The *triakis-octahedron*, {*hhk*}, where *h* is greater than *k*; 24 pyramid faces.

(vi.) The *icositetrahedron* or *trapezohedron*, {*hkk*}, where *h* is greater than *k*; 24 pyramid faces; *e.g.* leucite, $KAlSi_2O_6$, as {211}, and garnet as {211} alone or in combination with {110} as shown in fig. 16.

(vii.) The *hexakis-octahedron*, {*hkl*}, with 48 pyramid faces. Usually noticed in combination with other forms; *e.g.* garnet often exhibits {321} and fluorspar {421}.

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[1] *E.g.* the *cube* is one form in each of the classes belonging to the cubic system; but, crystallographically, 5 cubes, differing in symmetry, must be recognised. Thus a cube of pyrites is of a lower degree of symmetry than a cube of rock salt. Such differences of symmetry may at times be readily detected by examining the action of solvents upon the crystal faces. *Etched figures* are produced in this manner as definitely shaped depressions, their configuration being in accordance with the class symmetry of the crystal. Crystals of naturally occurring minerals sometimes exhibit on their faces similar natural markings, which indicate that the internal symmetry is not as high as the outward geometrical symmetry would at first sight suggest; *e.g.* pyrites.

[2] *E.g.* the + and − tetrahedra (p. 59). They may be distinguished when combined with other forms. When combined together, they are geometrically indistinguishable from an octahedron. Such a crystal, however, usually has one set of tetrahedral faces developed more than the other, and the fact that the two sets of faces differ in physical properties is often suggested by their appearance; *e.g.* zinc blende.

[3] It is commonly supposed that this optical activity, when limited to the crystalline state (e.g. *quartz*), arises from an enantiomorphous spiral grouping of the molecules in the crystal edifice; but that in the case of a substance which is optically active in the liquid or gaseous state (or in solution) the enantiomorphism is that of the atoms within the chemical molecule.

Class 31 (p. 54) *or the tetrahedrite class.*—The forms belonging to this class may be derived by hemihedrism from the holohedral forms. The

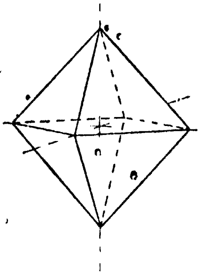

FIG. 10.—Octahedron.

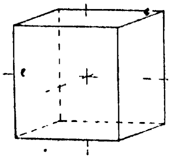

FIG. 11.—Cube.

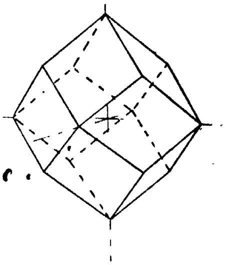

FIG. 12.—Rhombic dodecahedron

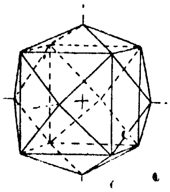

FIG. 13.—Tetrakis-hexahedron.

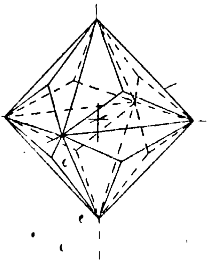

FIG. 14.—Triakis-octahedron.

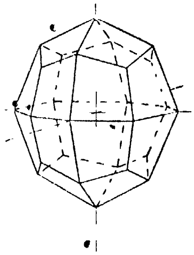

FIG. 15.—Trapezohedron.

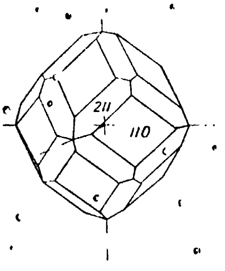

FIG. 16.—Garnet.

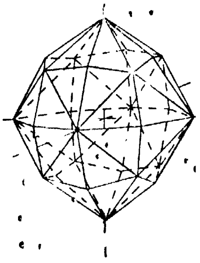

FIG. 17.—Hexakis-octahedron.

geometrically new forms are (figs. 18 to 22 respectively): (i.) the *tetrahedron* {111}; (ii.) the '*triakis-tetrahedron*, {*hkk*}; (iii.) the *deltoid-dodecahedron* {*hhk*}; and (iv.) the *hexakis-tetrahedron*, {*hkl*}, derived from the octahedron icositetrahedron, triakis-octahedron, and hexakis octahedron respectively.

There are two of each of the preceding forms, termed positive and egative respectively, and they may occur singly or in combination; in the tter case the combination is geometrically indistinguishable from a holo-

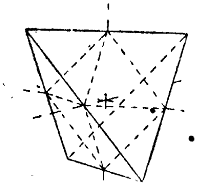
FIG. 18.—Positive tetrahedron.

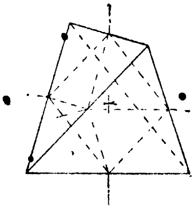
FIG. 19.—Negative tetrahedron.

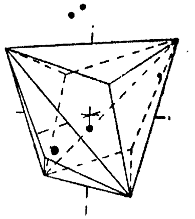
FIG. 20.—Triakis-tetrahedron.

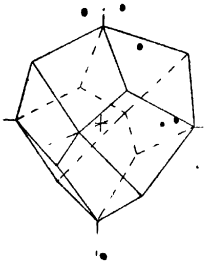
FIG. 21.—Deltoid dodecahedron.

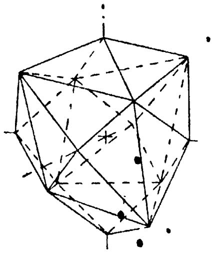
FIG. 22.—Hexakis-tetrahedron.

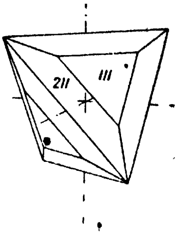

FIG. 23.

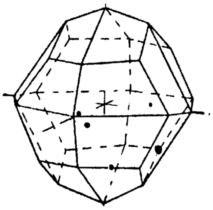
FIG. 24.—Diploid.

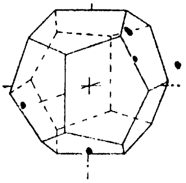
FIG. 25.—Pyritohedron.

hedral form. Figs. 18 and 19 represent the two tetrahedra and show their geometrical relationship to the octahedron.

Zinc blende, ZnS, and tetrahedrite, $4Cu_2S.Sb_2S_3$, are examples of (i.); tetrahedrite also occurs in the simple forms (ii.) and (iii.), while diamond sometimes occurs in the form (iv.). A combination of three forms, positive and negative tetrahedra and cube, is often found with boracite, $2Mg_3B_8O_{15}.MgCl_2$. A combination of (i.) and (ii.), occurring with tetrahedrite, is shown in fig. 23.

Class 30 (p. 54) *or the pyrites class.*—The forms of this class may also be derived from those of class 32 by hemihedrism, but by a method different from the preceding. The geometrically new forms are (i.) the *dyakisdodecahedron* or *diploid*, $\{hkl\}$, derived from the hexakisoctahedron, and shown in fig. 24; and (ii.) the *pentagonal dodecahedron* or *pyritohedron* $\{hk0\}$, derived from the tetrahexahedron and shown in fig. 25. These forms often occur on pyrites, FeS_2, and cobaltite, CoAsS.

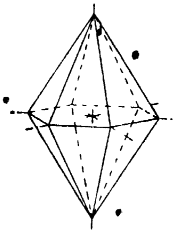

FIG. 26.—Hexagonal bipyramid, first order.

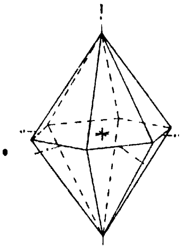

FIG. 27.—Hexagonal bipyramid, second order.

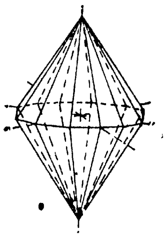

FIG. 28.—Dihexagonal bipyramid.

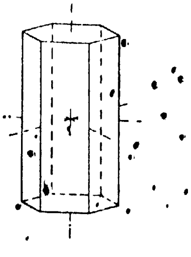

FIG. 29.—Hexagonal prism, first order.

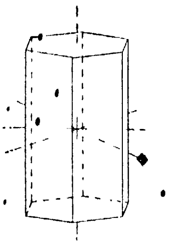

FIG. 30.—Hexagonal prism, second order.

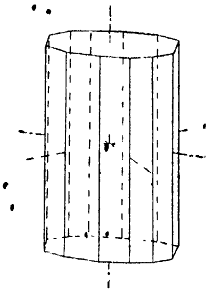

FIG. 31.—Dihexagonal prism.

Hexagonal System. *Holohedral class* (27, on p. 53).—The form $\{h0\bar{h}l\}$ constitutes the *hexagonal bipyramid of the first order*, which has 12 faces (fig. 26). The *hexagonal bipyramid of the second order*, $\{hh\overline{2h}l\}$, also has 12 faces, but is situated differently from the preceding with respect to the lateral axes (fig. 27). The most general form, $\{hi\bar{k}l\}$, is called the *dihexagonal bipyramid*, and has 24 faces (fig. 28).

The open *prism forms* corresponding with the preceding pyramids are

$\{10\bar{1}0\}$, $\{11\bar{2}0\}$, and $\{hi\bar{k}0\}$ respectively, with 6, 6, and 12 faces. They are shown in figs. 29, 30, and 31, terminated by *basal planes* $\{0001\}$.

Example: beryl, $Be_3Al_2(SiO_3)_6$. Fig. 32 shows a combination of $\{10\bar{1}0\}$, $\{10\bar{1}1\}$, and $\{0001\}$, frequently observed with beryl crystals.

Trigonal System (*rhombohedral*).—As has been previously mentioned, this system will be referred to hexagonal axes of reference, the vertical axis being always one of threefold symmetry.

Holohedral class (22 on p. 53).—The various forms are as follows (in addition to the hexagonal prism of the second order and the hexagonal bipyramid of the second order): (i.) the *positive* and *negative ditrigonal bipyramids*, $\{hi\bar{k}l\}$ and $\{\bar{h}\bar{i}kl\}$ respectively, each having 12 faces; (ii.) the *positive* and *negative trigonal bipyramids*, $\{h0\bar{h}l\}$ and $\{\bar{h}0hl\}$ respectively, each with 6 faces, (iii.) the *positive* and *negative ditrigonal prisms*, $\{hi\bar{k}0\}$ and $\{\bar{h}\bar{i}k0\}$, each with 6 faces; (iv.) the *positive* and *negative trigonal prisms*, $\{10\bar{1}0\}$ and $\{\bar{1}010\}$ respectively, each with 3 faces; and (v.) the *basal pinacoids* $\{0001\}$. It is very easy to deduce the nature of each of these forms.

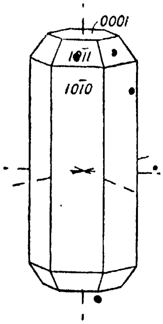

FIG. 32.—Beryl.

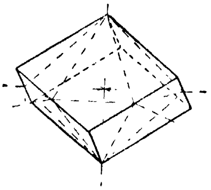

FIG. 33.—Positive rhombohedron.

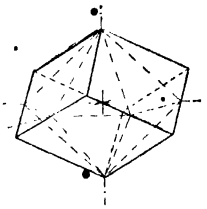

FIG. 34.—Negative rhombohedron.

This crystal class is not of much importance.

Class 21 (p. 53) *or the calcite class.*—The geometrically new forms of this important class are as follows: (i.) the *positive* and *negative rhombohedra*, $\{h0\bar{h}l\}$ and $\{0h\bar{h}l\}$ respectively, derived by hemihedrism from the hexagonal bipyramid and shown in figs. 33 and 34; and (ii.) the *positive* and *negative scalenohedra*, $\{hi\bar{k}l\}$ and $\{ih\bar{k}l\}$ respectively, similarly derived from the dihexagonal bipyramid. The positive form of the scalenohedron is shown in fig. 35.

Combinations of rhombohedra frequently occur. When one is positive and the other negative, the appearance of a bipyramid is presented. Two positive rhombohedra, differing in axial ratio, are often combined on the same crystal; *e.g.* calcite, $CaCO_3$. This mineral is also frequently found as rhombohedra, and as scalenohedra $\{21\bar{3}1\}$.

Class 18 (p. 53) *or the quartz class.*—This class exhibits forms geometrically different from the preceding in the *trigonal trapezohedra*, of which there are four: (*a*) *right positive*, $\{hi\bar{k}l\}$, (*b*) *left positive*, $\{k\bar{i}\bar{h}l\}$, (*c*) *right negative*, $\{\bar{h}\bar{i}kl\}$, and (*d*) *left negative*, $\{kihl\}$. The pair (*a*) and (*b*) are enantiomorphous; and so are the pair (*c*) and (*d*). On the other hand, the pair (*a*) and (*c*) are related to one another, like the two tetrahedra (p. 59) or rhombohedra (p. 61), being indistinguishable when moved out of position; and the pair (*b*) and (*d*) are similarly related. Form (*a*) is shown in fig. 36; it has six faces.

The preceding forms are only known in combination with other forms; *e.g.* quartz, SiO_2, which occasionally exhibits the trapezohedral faces; and cinnabar, HgS.

Class 20 (p. 53) *or tourmaline class.*—All crystals belonging to this class possess a polar axis, *i.e.* they are hemimorphous (p. 54), and exhibit pyro-electrical properties. The most important crystalline substance of this class is tourmaline, a complex borosilicate described in Volume IV. of this series.

Tetragonal System (*quadratic*). *Holohedral class* (15 on p. 53).—The three closed forms are the *tetragonal bipyramids* of the *first* and *second orders*,

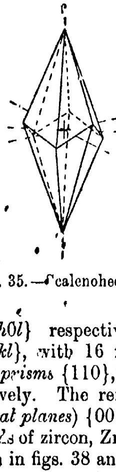

FIG. 35.—Scalenohedron.

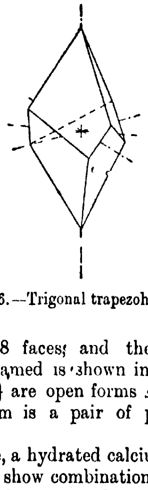

FIG. 36.—Trigonal trapezohedron.

$\{hhl\}$ and $\{h0l\}$ respectively, each with 8 faces; and the *ditetragonal bipyramid* $\{hkl\}$, with 16 faces. The last-named is shown in fig. 37. The *corresponding prisms* $\{110\}$, $\{100\}$, and $\{hk0\}$ are open forms of 4, 4, and 8 faces respectively. The remaining open form is a pair of pinacoid faces (known as *basal planes*) $\{001\}$.

The crystals of zircon, $ZrSiO_4$, and idocrase, a hydrated calcium aluminium silicate, shown in figs. 38 and 39 respectively, show combinations of the above forms. The forms are indicated by the symbols on typical faces.

It may be mentioned that in the classes 14 and 10 (pp. 52–53) of this system forms occur which may be derived from the tetragonal bipyramid by hemihedrism, and which may be likened to tetrahedra either drawn out or compressed along the vertical axis. They are called *positive* and *negative tetragonal sphenoids*, $\{hhl\}$ and $\{h\bar{h}l\}$ respectively, and may be observed on crystals of copper pyrites, $CuFeS_2$, and urea, $(NH_2)_2CO$.

Orthorhombic System (*rhombic*). *Holohedral class* (8 on p. 52).—The only closed forms are *bipyramids* (fig. 40), with 8 faces; the simplest or unit pyramid $\{111\}$ contains the fundamental face, and other pyramids $\{hkl\}$ are called *proto-*, *brachy-*, and *macro-pyramids*, according to the axis in the direction of which they are elongated. The *prisms* $\{hk0\}$ are open, vertical four-faced forms, the simplest being $\{110\}$; open, four-faced prism forms parallel to the lateral axes are either *brachydomes* $\{0kl\}$ or *macrodomes* $\{h0l\}$, the simplest being $\{011\}$ and $\{101\}$ respectively. The remaining forms consist of pairs of faces parallel to two axes; there are three pairs, the *basal pinacoid*, $\{001\}$, the *brachypinacoid*, $\{010\}$, and the *macropinacoid*, $\{100\}$.

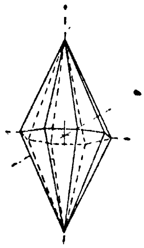

FIG. 37.—Ditetragonal bipyramid.

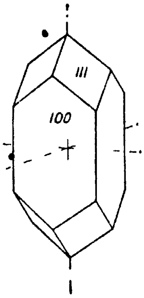

FIG. 38.—Zircon.

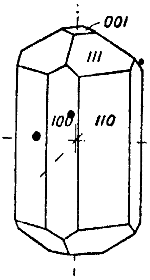

FIG. 39.—Idocrase.

The crystal of olivine, Mg_2SiO_4, shown in fig. 41, exhibits the following forms: prism (p), pyramid (o), macrodome (n), brachydome (q), macropinacoid (m), brachypinacoid (b), and basal pinacoid (c).

Class 6 (p. 52) is of interest as being the class to which rhombic sulphur belongs. Rhombic sulphur usually exhibits a pair of *positive and negative* *rhombic sphenoids*, $\{hkl\}$ and $\{hkl\}$ respectively. These sphenoids resemble distorted tetrahedra, and are enantiomorphous.

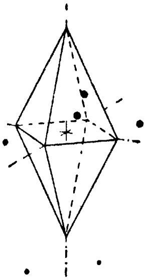

FIG. 40.—Orthorhombic bipyramid.

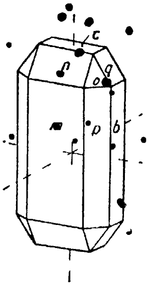

FIG. 41.—Olivine.

Class 7 (p. 52).—The crystals have a polar axis (p. 54); *e.g.* hemimorphite, $Zn_2(OH)_2(SiO_3)$.

Monoclinic System (*oblique*, or *monosymmetric*). *Holohedral class* (5 on p. 52).—All the forms are open. The *positive* and *negative hemipyramids* $\{hkl\}$ consist of 4 faces each. The *prisms*, $\{hk0\}$, and *clinodomes*, $\{0kl\}$ consist of 4 faces, but the *positive* and *negative orthodomes*, $\{h0k\}$, consist each of 2 parallel planes. The *basal-*, *ortho-*, and *clinopinacoids*, {001}, {100}, and {010} respectively, consist each of a pair of parallel faces. A positive hemipyramid is shown in fig. 42.

Examples: gypsum, $CaSO_4.2H_2O$; ferrous sulphate, $FeSO_4.7H_2O$; orthoclase, $KAlSi_3O_8$. The crystal of orthoclase shown in fig. 43 is a combination of prism (*p*), basal pinacoid (*b*), positive orthodome (*d*), and clinopinacoid (*c*).

Class 4 (p. 52) is of interest since it gives rise to enantiomorphous, *sphenoidal* forms.

Triclinic System (*anorthic* or *asymmetric*). *Holohedral class* (2 on p. 52).—Each form consists of a pair of parallel faces. There are four kinds of *quarter-pyramid*: $\{hkl\}$, $\{h\bar{k}l\}$, $\{\bar{h}\bar{k}l\}$ and $\{\bar{h}kl\}$; two kinds of *hemi-prism*: $\{hk0\}$ and $\{h\bar{k}0\}$; two kinds of *hemimacrodome*: $\{h\bar{0}k\}$ and $\{h0k\}$; two kinds of *hemibrachydome*, $\{0hk\}$ and $\{0h\bar{k}\}$; the *macropinacoid*, {100}; the *brachypinacoid*, {010}; and the *basal pinacoid*, {001}.

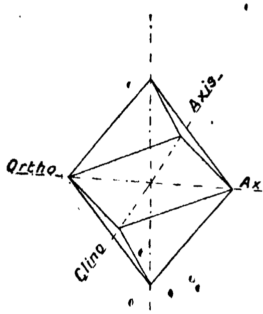

FIG. 42.—Positive monoclinic hemipyramid.

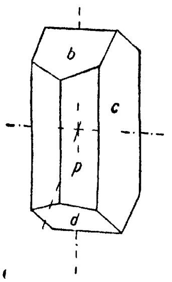

FIG. 43.—Orthoclase.

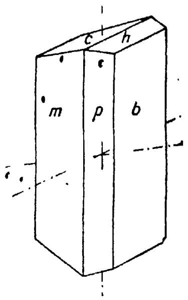

FIG. 44.—Potassium dichromate.

Examples: copper sulphate, $CuSO_4.5H_2O$; potassium dichromate, $K_2Cr_2O_7$. The latter is shown in fig. 44 (macropinacoid (*m*), brachypinacoid (*b*), basal pinacoid (*c*), hemibrachydome (*h*), and hemiprism (*p*)).

In *Class* 1 (p. 52) each face constitutes a separate form.

ALLOTROPY AND POLYMORPHISM.

Introductory.—If, upon examination, two substances prove to have exactly the same properties, physical and chemical, it is unhesitatingly assumed that they also have the same chemical composition. The converse is not true, however, for substances may be chemically identical although their physical properties are widely different. Ozone and oxygen are cases in point. It is with solid substances, however, that numerous instances of this phenomenon are to be found, both among elements and compounds. Attention was first drawn to this by Mitscherlich,[1] who showed that di-sodium hydrogen phosphate, $Na_2HPO_4.H_2O$, can exist in two distinct crystalline forms. Later, sulphur was observed to exist in different forms.[1] Other examples were speedily discovered.

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[1] Mitscherlich, *Ann. Chim. Phys.*, 1821, 19, 350.

When an elementary substance can exist in more forms than one, it is said to exhibit **allotropy** (Gk. *allos* another, *tropos* direction), the different varieties being termed the **allotropes** or **allotropic modifications.** Examples are furnished by sulphur, carbon, phosphorus, iron, tin, etc. In the case of compounds, however, the term **polymorphism** is used. A substance that can occur in two crystalline forms is said to be **dimorphous,** *e.g.* calcium carbonate; in three, **trimorphous,** *e.g.* tin[2]; in four, **tetramorphous,** *e.g.* ammonium nitrate[3]; and so on.

The term "polymorphism" is frequently used in connection with both elements and compounds in the crystalline state, but it does not include the allotropy of amorphous substances, such, for example, as that of ozone or of liquid sulphur.

Types of Polymorphism or Allotropy.—When the different polymorphous forms of any one substance are examined, it is found that each exists under a definite set of conditions of temperature and pressure. The physical properties of metals, for example, are susceptible to alteration according to the treatment to which they have been subjected. Thus Beilby[4] found that a metal can exist in two phases—namely, (1) the hardened or amorphous, (2) the annealed or crystalline. The former is convertible into the latter by heat, and the reverse change may be caused by pressure producing mechanical flow. Kahlbaum[5] and Kahlbaum and Sturm[6] found that the density of a specimen of metallic wire depends on the treatment to which it has been subjected, decreasing in many cases as the result of compression.[7] Subsequent annealing of the specimens causes a renewed increase of density. It is also known that the heat of solution of a metal and its behaviour in a voltaic cell depend on the treatment which it has previously undergone.[8]

But whilst these may be regarded as examples of polymorphism, another explanation is possible, for it is very probable that any deformation of a metal is a manifestation of *melting* produced by unequal strain, and that, with the removal of the strain the liquid portions do not immediately return to the crystalline, solid form.[9]

In other more definite instances of polymorphism the different varieties are found to have distinct and different physical properties. Each possesses its own crystalline form, melting-point, rate of expansion, conductivity for heat and electricity, colour, etc.; but although the chemical behaviour and reactivity are often dependent on the physical state of the substance, yet the ultimate products of chemical change are the same, as for example, in the combustion of the various forms of carbon with oxygen.

Three classes of allotropic or polymorphic substances exist.

1. *Enantiotropic Substances and Enantiotropy.*—The different forms of

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[1] Mitscherlich, *Ann. Chim. Phys.*, 1823, **24**, 264.

[2] Cohen and Goldschmidt, *Zeitsch. physikal. Chem.*, 1904, **50**, 225.

[3] Lehmann, *Zeitsch. Kryst. Min.*, 1877, **1**, 106.

[4] Beilby, *Proc. Roy. Soc.*, 1902, **72**, 218; *J. Soc. Chem. Ind.*, 1903, **22**, 1166; ***Phil. Mag.***, 1904, [vi.], **8**, 258; *Electro Chem. Metall.*, 1904, **3**, 806.

[5] Kahlbaum, *J. Chim. phys.*, 1901, **2**, 537.

[6] Kahlbaum and Sturm, *Zeitsch. anorg. Chem.*, 1905, **46**, 217; *cf.* Spring, ***Rec. trav. chim.***, 1904, **23**, 1.

[7] See also Spring, *Rec. trav. chim.*, 1904, **23**, 1.

[8] See, for example, Berthelot, *Compt. rend.*, 1901, **132**, 234.

[9] Johnston and Adams, *J. Amer. Chem. Soc.*, 1912, **34**, 563; Johnston, *ibid.*, 1912, **34**, 788.

many polymorphic substances can be transformed from one into the other at a definite temperature and pressure known as the transition-point, just as ice can be melted at 0° and water boiled at 100° under atmospheric pressure. In illustration of this the case of sulphur may be cited. This element can exist in a variety of different crystalline forms, of which the rhombic and monoclinic forms are the most important. At temperatures above 95·5° C. the latter is the stable variety, but when the temperature falls below 95·5° the monoclinic commences to change into rhombic sulphur. 95·5° C. is therefore known as the *transition temperature*, and at this point the two polymorphous forms are mutually transformable.

This type of polymorphism is termed *enantiotropic*, inasmuch as the polymorphous forms are directly interconvertible and exhibit a transition-point. The transition-point lies below the melting point of each form. Thus, rhombic sulphur melts at 112·8°, monoclinic at 119·2°.

The following is a list of well-marked cases of enantiotropic polymorphism among inorganic substances:—[1]

Substance.	Form and Transition-Point (°C).	Observer.
Fe	α-Fe → β-Fe, 770° β-Fe → γ-Fe, 890°	Tammann, *Zeitsch. anorg. Chem.*, 1903, **37**, 418.
S	Rhombic–monoclinic, 95·5°	Reicher, *Zeitsch Kryst. Min.*, 1884, **8**, 593.
Sn	Grey → tetragonal, 20° Tetragonal → rhombic, 170°	Cohen and Goldschmidt, *Zeitsch. physikal. Chem.*, 1904, **50**, 225.
NH_4NO_3	α-rhombic → β rhombic, 32·2°	Muller and Kaufmann, *ibid.*, 1903, **42**, 497.
	β rhombic → rhombohedral, 83° Rhombohedral → regular, 125·6°	Schwarz, *Beitrage zur Kenntnis der umkehrbaren Umwandlungen polymorphen Korper*, Gottingen, 1894.
SbI_3	Rhombic → hexagonal, 114°	Arzruni, *Beziehung zwischen Krystallform u. chem. Zusammensetzung*, Brunswick, 1898.
HgI_2	Tetragonal → rhombic, 127°	Reinders, *Zeitsch. physikal. Chem.*, 1900, **32**, 494.
KNO_3	Rhombic → rhombohedral, 129·5°	van Eyk, *ibid.*, 1905, **51**, 721.
AgI	Hexagonal → regular, 146°–147°	Steger, *ibid.*, 1903, **43**, 595.
$AgNO_3$	Rhombic → rhombohedral, 159·2°–159·7°	Schwarz, *loc. cit.*, also Hissink, *Zeitsch. physikal. Chem.*, 1900, **32**, 537.
$TlNO_3$	Rhombic → rhombohedral, 72·8° Rhombohedral → regular, 142·5°	van Eyk, *Zeitsch physikal. Chem.*, 1905, **51**, 721.

Much more is known of the relationship between enantiotropic forms than that between other types of polymorphous forms.

II. *Monotropic Substances and Monotropy*.—A number of substances exist in two or more forms which are not directly interconvertible and do not exhibit a transition-point. Thus, two varieties, called the α- and β-forms, of iodine monochloride are known, of which α-ICl melts at 27·2° and β-ICl at 13·9°, the former being the stable variety at ordinary temperature. Six varieties of sulphur are known which are not reversibly transformable one into another, in addition to the two well-known enantiotropic forms. The polymorphism in these cases is said to be *monotropic*, or irreversible.

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[1] See also Tammann and Huttner, *Zeitsch. anorg. Chem.*, 1905, **43**, 217.

It is possible that in the majority of cases monotropy arises from the fact that the transition-point is higher than the melting-point of either of the polymorphous forms at atmospheric pressure; and it is conceivable that by raising the pressure enantiotropy might be induced. In that case the same pair of polymorphs would exhibit monotropy or enantiotropy according to the pressure obtaining at the time.[1]

III. *Dynamic Allotropy.*—In the two preceding cases of solid polymorphic forms, the various varieties cannot exist in contact (except at a transition-point), one form always being stable, and the other, the metastable, tending to change into it. Quite different, however, is the behaviour of the two liquid forms of sulphur, known respectively as S_λ and S_μ, which exist together in equilibrium in definite proportions depending on the temperature.[2] The phenomenon is known as *dynamic allotropy*.

These two forms of liquid sulphur, of which S_λ is yellow and mobile, and S_μ brown and viscous, are present in molten sulphur, the amount of S_μ being small near the melting-point, but rising steadily with the temperature to a maximum of about 34 per cent at the boiling-point. The percentage of S_μ when equilibrium has been attained is as follows:—

$t°$	114·5°	130°	140°	154°	167°
S_μ	3·7	4·3	5·6	7·5	16·7

The freezing-point of sulphur accordingly varies with both the nature of the solid phase that separates and the percentage of S_μ in the liquid. Unless the liquid has been kept near the freezing-point for a sufficient length of time to enable equilibrium to be established, the percentage of the S_μ contained by it will vary according to circumstances. This type of allotropy is due to the existence of molecules of different complexity. Thus, in the case of sulphur, S_λ probably corresponds to the molecule S_8, and S_μ to S_6.[3]

Determination of Transition-Points.—All methods proposed for the determination of transition-points depend on the study of some particular physical property of the substance, which undergoes a marked change when the transition-point is reached.

1. *The Cooling Curve Method.*—If water be continuously cooled and the temperature be plotted against the time, the cooling curve so obtained (fig. 45) will show a horizontal portion where freezing occurs, corresponding to the fact that the temperature remains constant during a change of state.

Since at the transition-point a change of state also occurs, from one solid to another, a cooling curve of similar form may be expected, in which the horizontal portion will mark the transition-temperature. Such a curve is seen in fig. 46, which represents the results obtained by Osmond,[1] in determining the transition-points of the allotropic forms of iron.

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[1] Lehmann, *Molekularphysik* (Leipzig, 1888), vol. i. p. 194; Ostwald, *Zeitsch. physikal. Chem.*, 1897, **22**, 312; Schaum, *Die Arten der Isomerie* (Marburg, 1897).

[2] Smith, *Proc. Roy. Soc. Edin.*, 1902, **24**, 342; Smith and Holmes, *Zeitsch. physikal. Chem.*, 1903, **42**, 469; Smith, *Proc Roy Soc. Edin.*, 1905, **25**, 588 and 590; Smith, Holmes, and Hall, *Zeitsch. physikal. Chem.* 1905, **52**, 602; *J. Amer. Chem. Soc.*, 1905, **27**, 797; Smith and Holmes, *Zeitsch. physikal. Chem.*, 1906, **54**, 257; Hofmann and Rothe, *ibid.*, 1906, **55**, 113; Smith and Carson, *Proc. Roy. Soc Edin.*, 1906, **26**, 352; Carson, *J. Amer. Chem. Soc.*, 1907, **29**, 499; Smith and Carson, *Zeitsch. physikal. Chem.*, 1907, **61**, 200; Kruyt, *ibid.*, 1908, **64**, 513; Smith and Carson, *ibid.*, 1911 **77**, 661.

[3] Preuner and Schupp, *Zeitsch. physikal. Chem.*, 1909, **68**, 129; Beckmann and Liesche, *Zeitsch. anorg. Chem.*, 1913, **85**, 31. See Turner, *Molecular Association* (Longmans, 1915).

The dotted portion on the curve in fig. 45 represents a temporary state of supercooling previous to the separation of the stable phase. This supercooling often occurs during the process of finding both freezing-points and transition-points.

2. *The Dilatometric Method.*—In this method the rate of expansion with temperature is noted. The substance is contained in a dilatometer (a glass bulb with a long capillary stem), and covered with a liquid in which it is relatively insoluble. The stem is calibrated, and the rate noted at which the liquid expands as the dilatometer is slowly heated. At the transition-point there is a marked change in the rate of expansion, as indicated by the portion BC on the curve (fig. 47). Observations are repeated as the temperature slowly falls to the initial value.

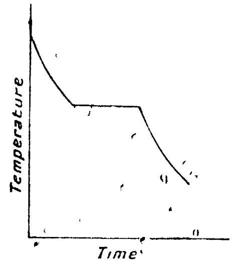

FIG. 45.—Cooling curve of water.

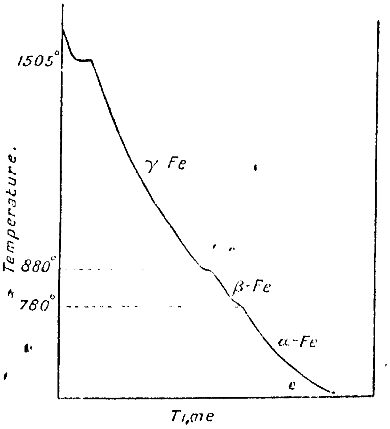

FIG. 46.—Cooling curve of iron.

A lag in undergoing transformation is usually observed, due to superheating when the temperature is being raised, or to supercooling if the temperature is being lowered, so that two branches, ABC and CDA, are obtained from which the mean value of the transition-point is calculated.

3. *The E.M.F. Method.*—If two pieces of the same metal in the same condition are immersed in an electrolyte and the metals connected together so as to form a closed circuit, no current passes, the E.M.F. of the cell being zero. If, however, the pieces of metal exist in different polymorphic forms, the cell has a definite, though small, E.M.F. At the transition-point,

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[1] Osmond, *Micrographische Analyse der Eisen-Kohlenstofflegierungen* (Knapp, Halle, 1906). See this series, Vol IX The view that iron can exist in three allotropic forms is by no means universally accepted, and has been made the subject of considerable discussion. See Benedicks, *J. Iron Steel Inst.*, 1912, II, 242; 1914, I, 407; Carpenter, *ibid.*, 1913, I, 315; Honda, *ibid.*, 1915, I., 199; Honda and Takagi, *ibid.*, 1915, II., 190; *Revue de Métallurgie*, 1913, 10, 1326; Burgess and Crowe, *J. Washington Acad. Sci.*, 1913, 3, 329. Also the General Discussion by the Faraday Society, November, 1915.

however, where the two forms are in equilibrium, the difference of potential between each metal and the solution is the same, and, since the potentials act in opposite directions, neutralise each other, the E.M.F. of the cell becoming zero.

Cohen and van Eyk[1] determined in this manner the transition-point of grey tin into the white or tetragonal variety. They employed a cell containing a strip of white tin and one of white tin whose surface had been transformed into grey tin, the electrolyte in the cell being ammonium stannic chloride. The cell was immersed in a bath the temperature of which was altered, until the E.M.F. was zero.

Other methods depend on a determination of the solubility (see p. 105); noting a change of colour, as in the case of mercuric iodide; watching, under the microscope, a change in crystalline form (the so-called optical methods); measuring the vapour pressure, as with salt hydrates; or determining the conductivity for heat or electricity.

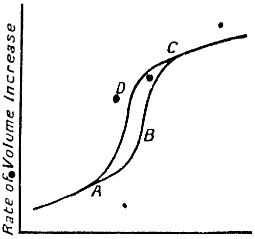

FIG. 47.—Dilatometric determination of transition-point.

Analogies between the Melting-Point and the Transition-Point.—The analogies between the melting-point and the transition point may be stated as follows:—

1. The transformation occurs at a perfectly definite temperature in both cases, and marks a change of state in either case.

2. Both melting-point and transition-point depend on the pressure.

An illustration of this has already been given in connection with the melting-point. The following table provides a similar illustration of the effect of pressure on the transition-point of rhombic and monoclinic sulphur.[2]

Transition-Point.	Pressure.	Transition-point.	Pressure.
95·5°	1 atmosphere	120·01°	638 kilos. per sq. cm.
100·11°	123 kilos. per sq. cm.	140·1°	1108 ,,
110·11°	391 ,,	150·1°	1350 ,,

The transition-point is like the melting-point, either raised or lowered, according to circumstances. In the case of sulphur, iron,[3] mercuric and silver iodides, the transition-point is raised by increasing the pressure. On the other hand, that of β-rhombic ammonium nitrate into the rhombohedral form is, like the melting-point of ice, lowered by pressure.

3. Heat is absorbed or evolved at the transition-point according to the direction of the change. The form stable at the higher temperature always

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[1] Cohen and van Eyk, *Proc. K. Akad. Wetensch. Amsterdam*, 1899, **2**, 77.

[2] Tammann, *Wied. Annalen*, 1899, **68**, 633.

[3] For iron, see Tammann, *Zeitsch. anorg. Chem.*, 1903, **37**, 448; for mercuric iodide, Lussana, *Nuovo Cimento*, 1895, [iv.], **1**, 405; for silver iodide, Tammann, *Wied. Annalen*, 1899, **68**, 633.

passes into that stable at lower temperature with evolution of heat (see Le Chatelier's Theorem, p. 178), and the reverse occurs during the heating process. Evidence of these facts is afforded by the horizontal portion always observed in the cooling curve. When β-Fe passes into α-Fe, a considerable amount of heat is disengaged, and the transition-point is widely known as the recalescence-point. There is therefore a latent heat of transformation just as there is a latent heat of fusion.[1]

4. Both melting-point and transition-point are affected by the presence of foreign substances, being as a rule lowered thereby. The presence of carbon in iron thus lowers the transition temperatures of (carbon) steels.

Moreover, the extent of the depression depends on the number of foreign molecules present, and not on the kind.[2]

Difference between Melting-Point and Transition-Point.—Any difference between melting-point and transition-point lies in the fact that the rearrangement of molecules of a solid consequent on a change of crystalline form must necessarily be slow compared with the rate at which a solid passes into the liquid form. It is well known that a liquid can be cooled considerably below its normal freezing-point. In like manner, monoclinic sulphur may be preserved for some time at temperatures far below its transition-point, and the same holds good for other substances, especially if cooled rapidly.

Any substance cooled below its transition-point remains for a time in what is known as the metastable state. Before the stable variety can be produced, the substance must pass through the unstable state, which can be best brought about by the addition of a trace of the form which is stable. The previously suspended transformation now immediately begins, for the metastable condition cannot be maintained in the presence of the stable phase of the substance. Transition from monoclinic to rhombic sulphur, on cooling, can therefore be assisted by the addition of a small amount of the rhombic form; as also the transformation of white into grey tin, which otherwise occurs only very slowly, at ordinary temperatures by adding a trace of grey tin. Not only may monoclinic sulphur be kept for a prolonged period below its transition-point without change occurring, but rhombic sulphur may just as readily be maintained above the transition-point without the transformation into monoclinic sulphur commencing; and this superheating is not peculiar to rhombic sulphur alone, but is exhibited by other substances. The superheating of a solid above its melting-point, however, is of very rare occurrence.[3]

CHEMICAL CRYSTALLOGRAPHY.

Isomorphism. Introductory. — That different chemical entities frequently yield very similar kinds of crystals has been known for many years. Thus in 1772 Romé de l'Isle was aware that mixed solutions of copper and ferrous sulphates will crystallise after the same form as those of pure ferrous sulphate, whereas a pure copper sulphate solution yields crystals of quite a different shape. In 1784 Leblanc drew attention to the fact that crystals of potassium aluminium sulphate may contain considerable quantities of iron and yet retain the same crystalline form; and in 1816 Gay-Lussac made the remarkable observation that a crystal of potassium alum will grow readily in a solution of ammonium alum, from which he concluded that the molecules must have a similar form. In 1819 Eilhardt Mitscherlich,[1] after a careful study of the arsenates and phosphates of certain metals, enunciated his famous **Law of Isomorphism**, according to which substances possessing "an equal number of atoms united in the same manner," exhibit complete identity of crystalline form. This law was at variance with the current view, originated by Haüy in 1784, that every substance of definite chemical composition is distinguished by its own particular crystalline form;[2] and it was soon found that Mitscherlich's law was only approximately true. Thus Mitscherlich himself had observed that the characteristic angles of di-ammonium hydrogen orthophosphate, $(NH_4)_2HPO_4$, and the corresponding arsenate, $(NH_4)_2HAsO_4$, differed by more than one degree, and numerous other examples of a similar nature were rapidly discovered. It has now been completely established, mainly through the extensive researches of Tutton, that Haüy's hypothesis is perfectly correct and that all the so-called isomorphous substances exhibit definite differences, although in many cases these differences are relatively small. It has further been shown that these differences are functions of the atomic weights of the elements concerned. At the same time Mitscherlich's principle of isomorphism, with a not too rigid interpretation, has proved, as will be seen presently, of great value to chemistry.

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[1] See Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, **43**, 215.

[2] Löwenherz, *Zeitsch. physikal. Chem.*, 1895, **18**, 70; Dawson and Jackson, *Trans. Chem. Soc.*, 1908, **93**, 344.

[3] For a discussion of polymorphism from the point of view of the Phase Rule, see Findlay, *The Phase Rule* (Longmans & Co.), 3rd edition, 1911. The reader may also consult Julius Meyer, *Die Allotropie der chemischen Elemente*, Stuttgart, 1910.

Recognition of Isomorphism.—Had the early belief of Mitscherlich that isomorphous bodies possess identical crystalline form proved to be correct, the recognition of isomorphism would have been an easy task; but from what has been said it will be evident that a mere study of crystalline form cannot of itself determine isomorphism. Thus, the ammonium phosphate and arsenate referred to above are regarded as isomorphous although their characteristic angles exhibit a difference of more than one degree. On the other hand, sodium nitrate and calcite have nearly the same crystallographic constants, but are not usually regarded as isomorphous. Similarly, substances crystallising in the regular system have the same crystallographic constants, but are not to be regarded as isomorphous unless, like the alums, they possess a similar chemical constitution. Again, it does not follow that substances must contain the same number of atoms in their molecules in order to be isomorphous, as was originally postulated by Mitscherlich. The ammonium salts, which have been made the subject of careful study by Tutton,[3] are cases in point, for "the replacement of the two atoms of potassium by the ten atoms of the ammonium groups is accompanied by an effect but slightly greater than that produced when two atoms of rubidium are substituted for those of potassium."[4]

The question naturally arises, therefore, as to what criterion is to be adopted in order to recognise isomorphism. According to Kopp[1] and Retgers,[2] two or more substances are to be regarded as isomorphous when they are capable of yielding *mixed crystals*—that is to say, crystals in which the components may be made to occur in varying proportions. It is not usually possible to obtain a complete series of mixed crystals of any two isomorphous substances, but it is often possible to obtain a limited series. This is the case with the chlorides of potassium and ammonium, mixed crystals being obtainable only when one of the components is in considerable excess of the other. The sulphates of potassium and ammonium, on the other hand, yield a very complete series of mixed crystals, which is all the more remarkable inasmuch as in ammonium sulphate the ten atoms of the two ammonium groups are equivalent to the two potassium atoms in potassium sulphate.

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[1] Mitscherlich, *Ann. Chim. Phys.*, 1820, 14, 172; 1821, 19, 350; 1823, 24, 264.

[2] Tutton, *Crystallography and Practical Crystal Measurement* (Macmillan & Co.), 1911, p. 5.

[3] Tutton, *Trans. Chem. Soc.*, 1894, 65, 628; 1903, 83, 1049; 1905, 87, 1123; 1906, 89, 1059. See also Murmann and Rotter, *Sitzungsber. K. Akad. Wiss. Wien*, 1858, 34, 135; Topsöe and Christiansen, *Ann. Chim. Phys.*, 1874, [v.], 1, 5; Perrot, *Arch. Sci. phys. nat.*, 1891, 25, 26.

[4] Tutton, *Trans. Chem. Soc.*, 1903, 83, 1073.

It is not to be supposed that mixed crystals are mere mechanical mixtures, for the recent work of Gossner[3] apparently proves the homogeneity of their structure, a conclusion that had already been indicated by the researches of Wulff;[4] but Gossner draws attention to the close connection existing between the power to form mixed crystals and the molecular volumes of the substances, and it appears that in an isomorphous series of substances only those members yield mixed crystals the molecular volumes of which are closely similar. Evidently, therefore, it is possible to have, on the one hand, isomorphous substances incapable of yielding mixed crystals and, on the other hand, mixed crystals from substances that are not truly isomorphous. Consequently Kopp and Retgers' criterion is inadequate, and, according to Tutton, "the term 'isomorphism' has remained to indicate the general similarity of the forms of the crystals of similarly constituted chemical substances, *the similarity of chemical constitution being, indeed,* the only *criterion of isomorphism which has remained valid.*"[5] This opinion, however, is not endorsed by all crystallographers, some of whom are prepared to regard substances as being isomorphous without making any reference to their chemical constitutions.[6]

But exceptions to Kopp and Retgers' rule are relatively uncommon, and in the absence of any direct chemical evidence, the power of forming mixed crystals or of exhibiting isomorphous overgrowth (*vide infra*) may be taken as indicating isomorphism. As recognised in this way, isomorphism has in the past proved very helpful in determining atomic weights (*vide infra*). It is usually considered necessary that two substances should belong to the same crystal *system* before they can be regarded as isomorphous, but they need not of necessity belong to the same class. In exceptional cases, however, it is possible to make out a good case for the isomorphism of substances belonging to different systems.[7]

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[1] Kopp, *Ber.*, 1879, **12**, 868.

[2] Retgers, *Zeitsch. physikal. Chem.*, 1889, **3**, 497. See also his numerous later papers in the same journal during the years 1889-96

[3] Gossner, *Zeitsch. Kryst. Min.*, 1907, **43**, 130.

[4] Wulff, *Zeitsch. Kryst. Min.*, 1906, **42**, 558.

[5] Tutton, *Crystalline Structure and Chemical Constitution* (Macmillan & Co.), 1910, p. 5. The italics are ours.

[6] See, *e.g.*, T. V. Barker (*Trans. Chem. Soc.*, 1912, **101**, 2484). It is then found that while in the majority of cases isomorphous substances have equal numbers of similar atoms in their molecules, *e.g.* K_2SO_4 and Rb_2SO_4, in a number of cases the molecules contain equal numbers of dissimilar atoms, *e.g.*, KIO_4 and $CaWO_4$, $NaNO_3$ and $CaCO_3$, $CuTiF_6.4H_2O$ and $CuCbOF_5.4H_2O$; and in other cases the molecules do not contain equal numbers of atoms, *e.g.* $(NH_4)_2SO_4$ and K_2SO_4, $(NH_4)_2SeO_4$ and Cs_2HgI_4, $MnCl_2.4H_2O$ and Na_2GlF_4.

[7] Fedorow, *Zeitsch. Kryst. Min.*, 1913, **52**, 11, 97.

Isomorphous Overgrowth.[1]—Mention has already been made of Gay-Lussac's observation that a crystal of potassium alum will readily grow in a saturated solution of ammonium alum and retain its same characteristic shape. This is known as isomorphous overgrowth, and was regarded by Kopp[2] as a reliable test for the isomorphism of any two or more substances. Like the power of yielding mixed crystals, however, that of exhibiting isomorphous overgrowth is possessed by bodies which are not necessarily isomorphous, but which have almost identical molecular volumes. Consequently this test is insufficient by itself, although in certain cases it may prove very useful.

When the molecular volumes of two isomorphous substances are approximately equal it is possible to obtain regular or "parallel" growths of one substance upon the other. For example, when a drop of a saturated solution of potassium permanganate is placed on a perfectly clean face of a crystal of potassium perchlorate and allowed to evaporate, numerous minute crystals of potassium permanganate are observed to form, having their corresponding edges arranged as nearly parallel to one another and to the corresponding edges of the perchlorate crystal as it is possible to expect when the slight angular differences between the permanganate and perchlorate are recalled.

The formation of isomorphous overgrowths or regular growths, then, are valuable indications of the existence of isomorphism.

Isopolymorphism.—It has been already observed (p. 65) that many substances are capable of existing in a variety of crystalline forms. Now, it frequently happens that two or more polymorphs of one substance are isomorphous with those of another. This phenomenon is known as isopolymorphism. When the number of isomeric polymorphs is two, the term *isodimorphism* is usually employed; if three, *isotrimorphism*. As might be expected, isodimorphism is the most usual type of isopolymorphism, and a good example of this is afforded by arsenious and antimonious oxides. For a long time these were only known in one form, each, and were not isomorphous, the arsenious oxide occurring in octahedra as the mineral *arsenolite*, and the antimonious oxide in rhombic crystals as the mineral *valentinite*. In view of the close chemical similarity between the two oxides this appeared remarkable, and it was to be presumed that other varieties of the two oxides existed isomorphous with those then known. In 1832 Wohler observed that arsenious oxide in the sublimate from a cobalt roasting furnace sometimes occurred as rhombic prisms, isomorphous with the usual rhombic antimonious oxide. Claudet likewise found the same modification in a Portuguese mineral, now known as *claudetite*. Finally, the mineral *senarmontite* was discovered, in which antimonious oxide occurs as octahedra, isomorphous with *arsenolite*. The two oxides are therefore isodimorphous.

A good example of isotrimorphism is afforded by the dioxides of tin (SnO_2) and titanium (TiO_2).

Isomorphous Series.—Elements that replace one another isomorphously in their compounds are termed "isomorphous elements," although it often happens that the free elements themselves are not isomorphous. Adopting this convention, it is possible to arrange the elements into ten isomorphous series. The following is Arzruni's[1] arrangement with one or two additions:—

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[1] Interesting contributions to this subject have been made by T. V. Barker (*Trans. Chem. Soc.*, 1906, 89, 1120; *Min. Mag.*, 1907, 14, 235; 1908, 15, 42), and for further information the reader is referred to his papers.

[2] Kopp, *Ber.*, 1979, 12, 868.

I. H, K, Rb, Cs, (NH_4), Tl; Na, Li, Ag.
II. Be, Zn, Cd, Mg, Mn, Fe, Os, Ru, Ni, Pd, Co, Pt, Cu, Ca, Sr, Ba, Pb.
III. La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er, Tm, Yb, Lu, Bi
IV. Al, Fe, Cr, Co, Mn, Ir, Rh, Ga, In, Tl.
V. Cu, Hg, Pb, Ag, Au.
VI. Si, Ti, Ge, Zr, Sn, Pb, Ce, Th, Mo, Mn, U, Ru, Rh, Ir, Os, Pd, Pt, Te (?).
VII. N, P, As, Sb, Bi, V.
VIII. Nb, Ta.
IX. S, Se, Cr, Mn, W; Te (?), As, Sb.
X. F, Cl, Br, I, Mn, (CN).

It will be observed that all the best known elements are included in this classification, save oxygen, carbon, boron, and scandium. Several of the elements appear in two or more series. Manganese is a case in point, occurring in series II., IV., VI., IX. and X., since its variable valency affords it special facilities for yielding different types of chemical compounds with correspondingly different crystalline structures. Thus, as divalent manganese in MnO we have isomorphism with CaO, FeO, etc. Trivalent manganese yields alums isomorphous with those containing aluminium and ferric iron, and so on. Further, the above grouping affords considerable support to the usually accepted periodic arrangement of the elements (see Chap. VIII.). Thus, the inclusion of silver in the first group of the periodic table is supported by the isomorphism of the sulphates and selenates of sodium and silver;[2] the isomorphism of the chromates and sulphates of several metals justifies the inclusion of chromium in the sixth group along with sulphur; and finally the isomorphous resemblance between $KClO_4$ and $KMnO_4$ indicates that manganese is correctly placed in the seventh group along with the halogens[3]

Isomorphism and Atomic Weights.—A study of isomorphism may be of assistance in determining the atomic weight of an element when its equivalent weight is known. Thus, for example, knowing the atomic weights of potassium and oxygen, analysis shows that the formula for potassium selenate is $K_2Se_nO_4$, where n is unknown.

Mitscherlich concluded, however, that potassium selenate and sulphate are isomorphous. From this it follows (knowing the formula for potassium sulphate) that in the former salt $n = 1$, only one atom of selenium being present. The formula is thus K_2SeO_4. Now, simple analysis shows that the salt contains 28·92 per cent. of oxygen and 35·79 per cent. of selenium. Hence for every 64 parts of oxygen (4 atoms) it contains $64 \times \frac{35{\cdot}79}{28{\cdot}92} = 79{\cdot}2$ parts of selenium (one atom). Thus the atomic weight of selenium is 79·2.

Classic examples of the application of the law of isomorphism to atomic weight determinations are afforded by Roscoe's correction of the atomic weight of vanadium (see Vol. VI.) and Lecoq de Boisbaudran's determination of the atomic weight of gallium (see Vol. IV.).

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[1] Arzruni, *Physikalische Chemie der Krystalle*, Vieweg, 1893; Groth, *Einleitung in die chemische Krystallographie*, Leipzig, 1904.

[2] Mitscherlich, *Pogg. Annalen*, 1828, **12**, 137.

[3] Mitscherlich, *ibid.*, 1832, **25**, 293.

BARLOW AND POPE'S THEORY OF VALENCY.

The researches of Sollas[1] have considerably widened our knowledge of the intimate structure of crystals, and paved the way for the enunciation by Barlow and Pope of a crystallographic theory of valency, which may be conveniently discussed at this point. According to Sollas, the space occupied by an atom of an element has the form of a solid of revolution, being in most cases spherical. On the outside of this atomic space a force of attraction exists, which tends to draw all other atoms towards the space; but such atoms are assumed to be incapable of penetrating or invading the atomic space by virtue of a repulsive force or pressure within. Equilibrium between the atoms of different elements implies the formation of a definite chemical molecule, and such molecules are largely dependent for their shape upon the number of their constituent atoms. Molecules containing similar numbers of atoms may thus be expected to possess similar configurations and hence exhibit certain crystallographic connections. Such, for example, is the case with the diatomic chlorides of sodium and potassium, which crystallise according to the cubic system and are characterised by cubical cleavage. Triatomic molecules, such as calcium fluoride, CaF_2, belonging to the cubic system exhibit octahedral cleavage, thereby indicating a different molecular structure.

Barlow and Pope[2] have developed these ideas more fully. By a crystal they understand "the homogeneous structure derived by the symmetrical arrangement in space of an indefinitely large number of spheres of atomic influence." The attractive forces acting between the atoms will cause the atomic spaces to lie in contact with one another at the maximum number of points, and the atoms composing a chemical molecule will, in consequence, be as closely packed together as possible, while the molecules themselves will also pack closely together into the minimum compass. When a number of similar bodies are packed with maximum closeness, they are usually found to have assumed a homogeneous arrangement. It is reasonable to suppose that crystals represent homogeneous structures of this kind, the units composing them consisting of atoms and molecules, and hence that these molecular structures coincide in symmetry and relative dimensions with the observed crystalline structures of the crystals. This is a most important assumption, inasmuch as theories regarding the arrangements of the atoms and molecules thereby admit of being checked quantitatively by reference to crystallographic constants.

The particular constants utilised by Barlow and Pope are termed *equivalence parameters*. They are denoted by x, y, z, and defined by the equations

$$x=\sqrt[3]{\frac{a^2W}{c\sin\alpha\,.\,\sin\beta\,.\,\sin\gamma}},\quad y=x/a,\quad\text{and}\quad z=cy,$$

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[1] Sollas, *Proc. Roy. Soc.*, 1898, 63, 270; 1902, 69, 294; 1908, 80, A, 267.

[2] Barlow and Pope, *Trans. Chem. Soc.*, 1906, 89, 1675; 1907, 91, 1150; 1908, 93, 1528; 1910, 97, 2308; see also Jaeger, *ibid.*, 1908, 93, 517; Jerusalem, *ibid.*, 1909, 95, 1275; Armstrong, *ibid.*, 1910, 97, 1578.

where a, b, c, α, β, γ are the crystallographic constants defined in the usual manner so that b is equal to unity (p. 49), and W is the valency volume of the molecule.[1]

The factor W, or valency volume, requires further definition. It is here that Barlow and Pope introduce a geometrical conception of valency. The sphere of influence of each atom in a molecule is assumed to be proportional to its valency, and is spoken of as its valency volume. Thus, the sphere of influence of each univalent element, such as sodium, potassium, chlorine, etc., is represented by a sphere of unit volume, although, as Barlow and Pope show, the spheres of influence of equi-valent elements are only approximately equal. Oxygen, of valency two, is represented by a sphere of twice, and carbon by a sphere of four times, the unit volume; and so on. The valency volume of a molecule is the sum of the valency volumes of the constituent atoms. In double salts a definite relationship obviously holds between the valency volumes of the several component parts and between that of each component and the total valency volume. These relationships in general are very simple. The alums provide one such example :—

	W.	W (total).
$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O.$	$12 + 36 + 96$	$= 144.$
$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O.$	$24 + 36 + 96$	$= 156.$

It should be emphasised that it is the relative volumes of the spheres of atomic influence of the atoms in a molecule that are supposed to be approximately proportional to the valencies of the atoms, the absolute magnitude of the sphere of influence of an atom changing considerably according to the molecule in which it finds itself.

The comparison of the crystalline structures of chemically allied substances is termed *morphotropy*. The comparison is usually carried out by reference to the *topic axial ratios*[1] of allied, isomorphous substances. Barlow and Pope, however, compare the *equivalence parameters*, even when the allied substances are not isomorphous, provided that the corresponding axial angles do not differ greatly. They find that when allied substances are thus compared, the corresponding equivalence parameters are frequently very nearly equal. In the absence of an equally good example amongst inorganic substances, the data for camphor and a number of its derivatives, as given by Barlow and Pope, may be quoted :—[2]

	x	y	z
Camphor	2·9943	3·4577	5·6021
α-dibromocamphor	2·9959	3·4949	5·5395
β dibromocamphor . . .	3·0107	3·4832	5·5308
α-π dibromocamphor . .	2·9498	3·4400	5·7156
β-monobromocamphor . .	2·9084	3·5382	5·6363

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[1] If distances x, y, z be measured along the crystallographic axes and regarded as the coterminous edges of a parallelopiped, the volume of this solid is equal to W. If, in the above equations, W be replaced by V, the gram-molecular volume, then the new values of x, y, z, usually denoted by χ, ψ, ω respectively, are called the *topic axial ratios* or the *molecular distance ratios* of the crystal (Becke, *Anzeiger K. Akad. Wiss. Wien*, 1893, **30**, 204; Muthmann, *Zeitsch. Kryst Min.*, 1894, **22**, 497; Tutton, *Trans. Chem. Soc.*, 1894, **65**, 628).

[2] Barlow and Pope, *Trans. Chem. Soc.*, 1906, **89**, 1685. It may be remarked that owing to the arbitrary manner in which the pyramid face (111) is often selected, and, in the case

The possibility of assigning almost the same sets of equivalence parameters to each member of a series of allied substances is held to be good evidence in favour of Barlow and Pope's original assumption concerning valency volumes

The phenomenon of isomorphism is explained by the equality of valency volume shown to exist between the replaceable constituents in a crystal. For, regarding a crystal as a homogeneous, closely packed assemblage of spheres of atomic influence, if similarly environed spheres or groups of spheres be removed, cavities are left which can be occupied by a different set of identical groups, provided their total volume is the same as that of the spheres removed, or so nearly the same as to require no alteration of the original arrangement of the spheres. That is to say, the valency volumes of the replaced and replacing groups must be nearly the same if the original form of the crystalline structure is to be preserved. An example is provided by the isomorphous compounds K_2SO_4, Rb_2SO_4, and Cs_2SO_4, and K_2SeO_4, Rb_2SeO_4, and Cs_2SeO_4, the equivalence parameters being practically the same for each series. Again, the isomorphism of the two substances *albite*, $NaAlSi_3O_8$, and *anorthite*, $CaAl_2Si_2O_8$, so different in composition, receives ready explanation In each case the total valency volume is 32, and NaSi in albite can be replaced by the group CaAl to produce anorthite without alteration of structure, because the valency volume of NaSi (namely 5) is equal to that of CaAl.

The explanation of the valency as a function of the volume in which the atom or group of atoms exerts an influence, proceeds from the results which Barlow and Pope obtained on examining the geometrical properties of assemblages of spheres. The first and simplest application, described in the preceding paragraph, explains equivalency and isomorphism. A second property discovered is that if a sphere of volume m is replaced by one of volume $m+n$, then any expansion of the assemblage brought about by the insertion of the sphere of larger volume does not require an alteration in the distribution of the spheres as a whole, provided that, in addition to the larger sphere, one or more spheres of total volume n are inserted at the same time. Close packing is, by such a process, restored without alteration of the original arrangement. Applied to chemical substitution, if for hydrogen, carbon of volume 4 is inserted, then 3 hydrogen atoms, or 1 nitrogen atom, or 1 hydrogen and 1 oxygen atom, must accompany the carbon atom, if alteration of structure is to be avoided. The valency relations between groups of elements is thus revealed, H being seen to be the equivalent of CH_3, of CN, or of OH. The close similarity of crystalline form between the chemically very different substances $NaNO_3$ and $CaCO_3$ is to be explained, according to Barlow and Pope, by this relationship. For if, in the rhombohedral structure of crystalline $NaNO_3$, Na of unit volume is replaced by Ca of volume 2, a gap is produced which can only be closed without alteration of the structure by the introduction of an additional valency volume. This is accounted for by the suggestion that N of volume 3 is replaced by C of volume 4, giving rise to calcite.

The multivalency which certain elements exhibit is explained somewhat

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of crystals of low grades of symmetry, to the arbitrary manner in which the directions of some or all of the crystallographic axes may be chosen, a certain amount of mathematical manipulation of published data is often necessary to bring out the resemblances. In the examples quoted above the derivatives of camphor are orthorhombic; camphor is hexagonal, but has, nevertheless, been referred to three mutually perpendicular axes.

similarly. For the replacement of an atom of valency m by one of valency $m+1$ necessitates another atom of valency 1 being inserted with it. Instead of the atom of valency $m+1$, the original atom of valency m together with an atom of valency 1 may be inserted. Thus, an atom of valency m may act as if it had a valency $m+1+1$ or $m+2$, while its sphere of influence retains the volume appropriate to an atom of valency m.

Similarly, if two atoms of valency 1 are forced into the cavity with the original atom of valency m, one or more atoms of total valency 2 must be inserted to preserve close packing without rearrangement. In this case, the original atom of valency m functions as of valency $m+4$. Thus an explanation is afforded of the fact that the several valencies of multivalent elements generally differ by two or multiples of two (p. 285), as in the polyiodides, *e.g.* CsI, CsI_3, CsI_5, CsI_7, and CsI_9.

A further discussion of Barlow and Pope's theory cannot be attempted here, but it should be pointed out that numerous objections to this as to every other theory of valency may be brought forward.[1]

THE COLLOIDAL STATE.[2]

Introductory.—If a dilute solution of sodium silicate is poured into an excess of hydrochloric acid, no precipitate is formed. When, on the other hand, concentrated hydrochloric acid is mixed with a concentrated solution of sodium silicate a white gelatinous mass of silicic acid is produced. An obvious explanation is that the silicic acid is but sparingly soluble in water and, whilst not readily precipitated from dilute solution, it separates out if concentrated. After studying the problem, Graham[3] came to the conclusion that such an explanation was untenable; for, on pouring the dilute solution of silicic acid into a small dish made of parchment and floating it in water, he discovered that while the sodium chloride diffused through into the water below, the silicic acid remained behind in the dish, thus proving that it was not an ordinary aqueous solution. In view of this, Graham termed silicic acid a *colloid*.[4] Sodium chloride, and all other similar bodies that were capable of diffusion through parchment were called *crystalloids*, and the method of separating crystalloids from colloids by diffusion was termed *dialysis*.

A colloidal solution is usually termed a *sol*. If water is the liquid medium, the solution is known as a *hydrosol*: if alcohol, an *alcosol*; if glycerine, *glycerosol*; or the more general term *organosol* is employed when the medium consists of some organic liquid. All liquid media in colloidal solutions are known as *dispersion media*, whilst the colloidal substance itself is termed the

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[1] T. V. Barker, *Trans. Chem. Soc.*, 1912, **101**, 2484; 1915, **107**, 744; T. W. Richards, *J. Amer. Chem. Soc.*, 1913, **35**, 381; 1914, **36**, 1686. Compare Barlow and Pope, *ibid.*, 1914, **36**, 1675, 1694.

[2] The literature on this subject is very voluminous, and the reader wishing to pursue the study further is recommended to consult the following works:—

Poschl, *The Chemistry of Colloids*, trans. by H. Hodgson (Griffin & Co., 1910); Wo. Ostwald, *Grundriss der Kolloidchemie* (Dresden, 1909); A. Müller, *Allgemeine Chemie der Kolloide* (Leipzig, 1907); Zsigmondy, *Über Kolloidchemie* (Leipzig, 1907); Proctor, *Colloidal Chemistry* (*Brit. Assoc. Rep.*, 1908, or *Chem. News*, 1908, **98**, 152); and *Zeitschrift für Chemie und Industrie der Kolloide*, edited by Wo. Ostwald, Leipzig. Hatschek, *Introduction to the Chemistry and Physics of Colloids* (Churchill & Co., 1913); Burton, *The Physical Properties of Colloidal Solutions* (Longmans & Co., 1916); Ostwald, *Colloid Chemistry*, translated by Fischer (Churchill & Co., 1916).

[3] Graham, *Phil. Trans.*, 1861, **51**, 204; *Annalen*, 1862, **121**, 1; Ostwald's *Klassiker*, No. 179 (1911).

[4] From Gk. κολλα, glue.

disperse phase. It is not necessary that the medium shall be a liquid; for colloidal solutions in solid media are known, such as of gold in glass.[1]

General Occurrence of the Colloidal State.—So many colloidal substances have now been prepared, among them many substances which exist ordinarily as crystalloids, that the colloidal state may be regarded as a general state of matter into which all solid substances, under suitable conditions, may be brought. The earliest studied colloids were largely of organic character, such as white of egg, gum arabic, dextrin, caramel, etc.

Substances yielding Colloidal Solutions.—Besides numerous organic bodies the following inorganic substances yield colloidal solutions:—[2]

1. *The elements*: phosphorus, sulphur, selenium, silicon, and boron, together with almost all the metals.

2. *Sulphides* of selenium, tellurium, tungsten, arsenic, antimony, bismuth, zinc, cadmium, tin, lead, iron, cobalt, nickel, copper, iridium, mercury, silver, gold, palladium.

3. *Oxides and hydroxides*: phosphoric acid, silicic acid, arsenic acid; magnesium, lanthanum, and yttrium hydroxides. Hydroxides of glucinum, aluminium, zirconium, thorium, titanium, tungsten, molybdenum, chromium, manganese, cerium, didymium, erbium, bismuth, tin, lead, copper, iron, gold, cobalt, nickel, silver, mercury. Oxide of barium and vanadium pentoxide.

4. *Salts, etc.*: Chlorides of sodium and lead, mercurous chloride, sodium carbonate. Sulphate, phosphate, chromate and carbonate of barium. Molybdenum blue, tungsten blue, gold purple, Berlin blue, copper ferrocyanide.

Since 1907 many other inorganic substances have been prepared in the colloidal state, among them graphite,[3] sodium bromide and iodide, and potassium chloride, bromide, and iodide.[4]

Preparation of Colloidal Solutions.—Colloidal solutions of inorganic substances may be prepared in a variety of ways, of which the following are typical:—

I. *Elements*.—(*a*) By the action of many reducing agents, such as tannic acid, pyrogallol, a solution of phosphorus in ether, formaldehyde, hydrazine hydrate, hydroxylamine, etc., on very dilute solutions of metallic salts (*e.g.* of gold and silver).

(*b*) By the addition to the disperse medium of a small quantity of a solution of the substance in another solvent. Thus, colloidal sulphur or phosphorus may be prepared very simply by adding a solution of the element in alcohol to a large bulk of water.[5]

(*c*) By an electrical discharge under pure water between poles of the metal or other element.[6] In this way colloidal Ag, Pt, Au, Cd, Se, and S have been prepared.

(*d*) By the disintegrating action of ultra-violet light on the element, which is covered by the disperse medium (*e.g.* Ag, Cu, Sn, Pb)[7]

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[1] According to Tammann's view of the amorphous state (p. 47), glass is a supercooled liquid.

[2] See P. Rohland, *Kolloid Zeitsch.*, 1907, 2, 53.

[3] Acheson, *J. Franklin Inst.*, 1907, 164, 375.

[4] Paal and Kühn, *Ber.*, 1908, 41, 51 and 58; Paal and Zahn, *ibid.*, 1909, 42, 277 and 291.

[5] von Weimarn and Maljisheff, *J. Russ. Phys. Chem. Soc.*, 1910, 42, 481; von Weimarn and Kagan, *ibid.*, 1910, 42, 480.

[6] Bredig, *Zeitsch. angew. Chem.*, 1898, p. 951; Bredig and Muller von Berneck, *Zeitsch. physikal. Chem.*, 1899, 31, 258; Bredig, *ibid.*, 1900, 32, 127; Müller and Nowakowski, *Ber.*, 1905, 38, 3779.

[7] Svedberg, *Ber.*, 1909, 42, 4375; *Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 129.

(*e*) By stirring the finely divided element with an aqueous solution of an organic colloid (*e.g.* graphite with tannic acid).[1]

II. *Hydroxides.*—(*E.g.* $Fe(OH)_3$ and $Al(OH)_3$.) By hydrolysis. A colloidal solution of ferric hydroxide, for example, is readily prepared by adding 5 c.c. of 33 per cent. ferric chloride solution to a litre of boiling water, and removing the chloride remaining, as well as the hydrochloric acid, by dialysis.

III. *Sulphides.*—(*E.g.* As_2S_3 and Sb_2S_3.) By the passage of sulphuretted hydrogen through certain solutions; for example, a solution of arsenious oxide in water.[2]

IV. *Salts.*—By chemical interaction in organic solvents. Thus, colloidal sodium chloride has been prepared by the interaction of ethyl-chloro-acetate and sodio-ethylmalonate in benzene or ether.[3]

The solutions so prepared are in most cases very dilute. It is possible to separate the colloidal substance by centrifuging the solution and filtering, or by special filtration processes (see p. 81), and the solid substance so obtained may be again converted into a colloidal solution by shaking with the dispersion medium.

In appearance, sols may appear clear, turbid, opalescent, or fluorescent according to their nature and the mode of preparation. The metallic hydrosols often exhibit beautiful colours, as, for example, the famous "Purple of Cassius,"[4] and the various forms of colloidal silver.[5]

Nature of Colloidal Solutions. Solution or Suspension?—The question whether any supposed solution is a true solution or only a suspension may be tested in various ways, such as by allowing the liquid to stand for some time, by filtration, by microscopical examination, and by Tyndall's method. The last-named test consists in passing a powerful beam of light through the solution, and its efficacy depends on the fact that if a space, whether liquid or gaseous, is devoid of suspended particles, the beam is not seen during its actual transmission through the medium. When particles are present, the beam is rendered visible, a glow being apparent in the liquid, and, on emergence, the light is found to be polarised. Picton and Linder[6] found that colloidal solutions could be preserved as such for a long time, that they could be passed unchanged through filter paper, and in most cases were quite void when examined under the microscope. The Tyndall test, however, clearly showed the preparations to be only suspensions. An ingenious application of Tyndall's method was made by Siedentopf and Zsigmondy[7] in the construction of the ultra-microscope, in which a very powerful beam of light, either from an arc lamp or from the sun, is concentrated on and made to pass through a little of the sol contained in a small quartz cell. Through a microscope the line of vision of which is at right angles to the beam of light, the particles present are seen by means of the light they reflect, and their size and number can be estimated. By means of the ultra-microscope colloidal solutions, of inorganic substances, at any rate, have been proved to consist of suspensions of particles in very fine, but varying states of division.

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[1] Acheson, *loc. cit.*

[2] Picton and Linder, *Trans. Chem. Soc.*, 1892, 61, 137 and 148.

[3] Paal and Kuhn, *loc. cit.*

[4] See Vol. II. of this series.

[5] See Carey Lea, *Kolloides Silber und die Photohalide* (Dresden, 1908).

[6] *Loc. cit.*

[7] Siedentopf and Zsigmondy, *Ann. Physik*, 1903, [iv.], **10**, 1; Siedentopf, *J. Roy. Micros. Soc.*, 1903, p. 573; Zsigmondy, *Versammlung deutscher Naturforscher*, Rep. 85 (Wien) Siedentopf, *Kolloid-Zeitsch.*, 1913, **12** 68.

The Size of Colloid Particles.—Various methods have been devised for the determination of the approximate size of the particles in colloidal solutions. Two of these are described here.[1]

(*a*) *Ultra-Filtration.*—Bechhold[2] has constructed a series of filters of different degrees of efficiency and measured the sizes of the pores they contain. The filters were made by soaking filter papers either in a solution of collodion in acetic acid, afterwards washing with water, or in gelatine (of various concentrations) which was subsequently hardened by formalin. Such filter papers possessed pores of diameter varying between 930 and 21×10^{-6} mm., and by their use, Bechhold was able to classify the various colloids according to the sizes of their particles. In the following table the colloids are arranged in order according to the sizes of their particles, the largest being placed first:—[3]

CLASSIFICATION OF COLLOIDS BY SIZE.

(Ultra-Filtration Process).

Colloidal Platinum.
„ Ferric Hydroxide.
„ Arsenious Sulphide.
„ Gold.
1 per cent. Gelatine.
Colloidal Silicic Acid.
Litmus.
Dextrin.
Crystalloids.

(*b*) *By the Ultra-Microscope.*—The way in which this may be done can be best illustrated by an example studied by Burton.[4] A solution o colloidal silver containing 6·8 mgms. silver per 100 c.c. was diluted one hundred times. Of this solution, 0·01 c.c. was examined in an instrument working on the same principle as the ultra-microscope, and the number of particles counted, this number being 300 Assuming the particles to be spherical and the specific gravity of silver to be 10·5, the average radius of the particles was found to be $1 \cdot 7 \times 10^{-5}$ cm. The average size of the particles in colloidal solutions of platinum, gold, and silver, was found to be 2×10^{-5} to 6×10^{-5} cm.

The smallest particle capable of being detected under the most favourable conditions (bright sunlight) in the ultra-microscope has a diameter of 4×10^{-6} mm. In comparison with this, the following molecular diameters calculated on the basis of the kinetic theory furnish an interesting comparison:—

Chloroform . . .	$0 \cdot 8 \times 10^{-6}$	mm.
Ethyl alcohol . . .	$0 \cdot 4 \times 10^{-6}$	„
Carbon dioxide . . .	$0 \cdot 28 \times 10^{-6}$	„
Hydrogen . . .	$0 \cdot 1 \times 10^{-6}$	„

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[1] For other methods see V. Henri, *Trans. Faraday Soc.*, 1913, **9**, 47.

[2] Bechhold, *Zeitsch. physikal. Chem.*, 1907, **60**, 257.

[3] An earlier process used for a similar purpose by Picton and Linder consisted in filtering the liquid through porous clay cells.

[4] Burton, *Phil. Mag.*, 1906, [vi.], **11**, 425.

The range of vision of the ordinary microscope is limited to particles of sizes ranging from 400×10^{-6} to 800×10^{-6} mm.

It is possible to obtain some idea of the size of colloidal particles by a study of the freezing-points and of the osmotic pressures exerted by colloidal solutions. From freezing-point determinations it has been calculated that the molecular weight of ferric hydroxide ranges from 4900 to 5400 in solutions containing from 2·6 to 1·16 per cent. of colloid; whilst silicic acid yields an even higher result for its molecular weight. The practical difficulty in carrying out these experiments, however, lies in the extreme smallness of the observed osmotic pressure and freezing-point depression, in consequence of which small errors due to the presence of traces of impurity exert an unduly large effect upon the accuracy of the results.[1]

The Motion of Colloid Particles. The Brownian Movement.—In 1827 Robert Brown, a botanist, observed that minute particles exhibit a peculiar vibratory motion when suspended in a liquid. This Brownian movement, as it is called, is characteristic of colloidal solutions and can be readily observed by means of the ultra-microscope. The movement is slow, persistent, and irregular, as is well seen by photographing the movements on a cinematograph film;[2] it is independent of such conditions as vibration, intensity of illumination and convection currents; and seems to depend only on the size of the particles and upon the temperature and viscosity of the fluid in which they are suspended.[3]

It was suggested by Wiener and others that the Brownian movements are to be attributed to the molecular motion of the fluids, of which the particles thus act as indicators. This suggestion was developed by Einstein[4] into a mathematical theory, capable of experimental verification without reference to the actual velocities of the particles. The correctness of the theory has been strikingly demonstrated by the experiments of Perrin upon suspensions of gamboge and mastic in water, glycerol, and aqueous solutions of sucrose, urea, and glycerol; and by the subsequent work of Millikan, Svedberg, Seelis, Nordlund, and others.[5]

The study of Brownian movement is therefore of great theoretical importance. Not only does it afford most striking evidence of the reality of molecules, but it enables the value of **Avogadro's Constant**, *i.e.* the number of molecules (N) present in a gram-molecule of gas, to be determined. The evaluation of this constant has been effected by Perrin in four distinct ways, each based upon the theory of the Brownian movement. The results, which were closely concordant, and in good agreement with the values derived from totally different theoretical considerations, lead to the conclusion that $N = 70 \cdot 5 \times 10^{22}$. Other observers have obtained the following results for N: Millikan, $60 \cdot 6 \times 10^{22}$; Svedberg and Inouye, $62 \cdot 0 \times 10^{22}$; Seelis, 72×10^{22}; Nordlund, $59 \cdot 1 \times 10^{22}$.

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[1] See Gladstone and Hibbert, *Phil. Mag.*, 1889, [v.], **28**, 38; Lillie, *Amer. J. Physiol.*, 1907, **20**, 127; Moore and Roaf, *Biochem. J.*, 1906, **2**, 34; Linebarger, *Amer. J. Sci.*, 1892, [iii.], **43**, 218.

[2] V. Henri, *Compt. rend.*, 1908, **146**, 1024; **147**, 62.

[3] Wiener, *Pogg. Annalen*, 1863, **118**, 79; Jevons, *Proc. Manchester Lit. Phil. Soc.*, 1869, **9**, 78; *Chem. News*, 1871, **21**, 66; Gouy, *J. de Physique*, 1888, **7**, 561.

[4] Einstein, *Ann. Physik*, 1905, [iv.], **17**, 549; 1906, [iv.], **19**, 287, 371; 1907, [iv.], **22**, 569; Smoluchowski, *ibid.*, 1906, [iv.], **21**, 756; Langevin, *Compt. rend.*, 1908, **146**, 530.

[5] Perrin, *Compt. rend.*, 1908, **146**, 967; 1908, **147**, 475; 1909, **149**, 475, 530; 1911, **152**, 1380, 1569; *Ann. Chim. Phys.*, 1909, [viii.], **18**, 5. (A translation, by Soddy, of the memoir in the *Annales* has been published by Taylor & Francis, 1910); Shaxby and Emrys-Roberts, *Proc. Roy. Soc.*, 1914, **A**, **89**, 544; Millikan, *Physikal. Zeitsch.*, 1913, **14**, 796; Svedberg and Inouye, *Arkiv Kem. Min. Geol.*, 1911, **4**, No. 19; Seelis, *Zeitsch. physikal. Chem.*, 1914, **86**, 682; Nordlund, *ibid.*, 1914, **87**, 40; Iljin, *ibid.*, 1914, **87**, 366; Svedberg, *Die Existenz der Moleküle* (Leipzig, 1912).

The Electrical Properties of Colloidal Solutions. Cataphoresis. Precipitation or Coagulation of Colloids.—If a glass tube about 30 cm. in length be bent into the shape of a V, filled with a colloidal solution of arsenious sulphide and a current at 60 volts be passed from platinum electrodes through the solution, in the course of an hour the liquid round the negative pole will be found quite clear and the clear space will gradually extend down the tube as time elapses. The arsenious sulphide is found deposited on the positive pole. Evidently the colloidal arsenious sulphide particles must be negatively electrified. This phenomenon, which is called either "electrical osmose" or "cataphoresis," was found by Picton and Linder[1] to be of general occurrence, some colloids being negatively, others positively electrified. The following table gives the electrical character of a number of colloids suspended in water:—

Electro-Positive.	*Electro-Negative.*
Ferric Hydroxide.	Arsenious Sulphide.
Chromium Hydroxide.	Antimony Sulphide.
Bismuth.	Platinum.
Lead.	Gold.
Zinc.	

The polarity depends not only on the disperse phase, but also on the disperse medium. Thus, the metallic hydroxides and silicic acid are charged positively when in water, but negatively in turpentine.

The fact that the colloidal particles carry definite charges is strikingly brought out in the study of their precipitation or coagulation, which can be brought about by the addition of very small quantities of electrolytes. In the following table, prepared by Freundlich,[2] the minimum concentrations of various salt solutions required to produce complete coagulation of As_2S_3 after two hours are recorded, the concentrations being expressed in gram-molecules per litre of solution, except for K_2SO_4, H_2SO_4, and $Ce_2(SO_4)_3$.

Electrolyte.	Concentration.	Electrolyte.	Concentration.
LiCl	0·0815	$CaCl_2$	0·000905
NaCl	0·0712	$Ca(NO_3)_2$	0·00095
KCl	0·0691	$BaCl_2$	0·00096
$\frac{1}{2}K_2SO_4$	0·0915	$ZnCl_2$	0·00096
NH_4Cl	0·0591	$AlCl_3$	0·00013
HCl	0·0129	$Al(NO_3)_3$	0·00014
$\frac{1}{2}H_2SO_4$	0·0120	$\frac{1}{2}Ce_2(SO_4)_3$	0·00013
$MgCl_2$	0·0010	$Th(NO_3)_4$	0·00013

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[1] Picton and Linder, *Trans. Chem. Soc.*, 1892, 61, 148; 1897, 71, 568.

[2] Freundlich, *Zeitsch. physikal. Chem.*, 1903, 44, 129.

These figures clearly prove what Schulze[1] had previously found, that the precipitating effect on a negatively charged colloid is dependent on and increases with the valency of the positive ion; also, that the precipitating agents which yield the greatest concentrations of ions at a given dilution are most effective, so that the mineral acids have a much greater precipitating power than the organic acids. In analytical chemistry the formation of colloidal solutions of arsenious and antimony sulphides is prevented by passing hydrogen sulphide into solutions acidified with hydrogen chloride

While the precipitation of the negatively charged colloid is dependent on the positive ion of the added electrolyte, the positively charged colloid, as might be expected, is influenced mainly by the valency of the negative ion,[2] as the following figures for ferric hydroxide show :—

Electrolyte.	Concentration.	Electrolyte.	Concentration.
NaCl . . .	0·00925	K_2SO_4 . . .	0·00020
$\frac{1}{2}BaCl_2$ . . .	·00964	$MgSO_4$ . . .	·00022
KNO_3 . . .	·0119	$K_2Cr_2O_7$ . . .	·00019
$\frac{1}{2}Ba(NO_3)_2$ . .	·0110		

Here the divalent negative ions are much more effective than the monovalent.

Finally, as might be presumed possible, two oppositely charged colloids can precipitate one another. This was proved by Biltz,[3] who showed that arsenious sulphide is precipitated by the addition of ferric hydroxide hydrosol, the precipitate or gel containing both substances since the electrical charge of each is neutralised by that of the other.

From what has been said, it will appear that a colloidal solution or suspension only remains as such so long as the particles are electrically charged.

Adsorptive Power of Colloids.—When a colloid is precipitated from its solution or suspension by an electrolyte, the precipitate always contains a definite amount of the ion to the specific influence of which precipitation is due, the quantity retained being proportional to the equivalent of the ion. Thus, Whitney and Ober[4] found that the precipitate obtained by the action of barium chloride solution on arsenious sulphide sol had the composition $90As_2S_3 + 1Ba$, the barium being present as hydroxide. When this precipitate in turn was washed with calcium or strontium salts, the barium was replaced by equivalent quantities of these metals. As the coagulum contains the positive ion, which cannot be removed by washing with water, the liquid becomes acid in character and the acidity can be determined by titration. The phenomenon, which was first noticed in colloids by Linder and Picton,[5] is known as *adsorption*, and in character is very similar to the adsorption of gases by charcoal (see Chap. III.). For any given substance, the extent of adsorption is connected with the concentration of the precipitating electrolyte by the following formula:—

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[1] Schulze, *J. prakt. Chem.*, 1882, **25**, 431; 1883, **27**, 320.

[2] Hardy, *Zeitsch. physikal. Chem.*, 1900, **33**, 385.

[3] W. Biltz, *Ber.*, 1904, **37**. 1095.

[4] Whitney and Ober, *J. Amer. Chem. Soc.*, 1901, **23**, 842; *Zeitsch. physikal. Chem.*, 1902, **39**, 630.

[5] Linder and Picton, *Trans. Chem. Soc.*, 1895, **67**, 63.

$$C_a = \beta C_b^{\frac{1}{p}},$$

where C_a and C_b denote the concentrations of the electrolyte in the precipitated colloid and the solution respectively; β and p are constants, to be determined by experiment, for any given temperature.

Differences between Organic and Inorganic Colloids.—The properties of colloids which have been described above are mainly those of inorganic colloids. Organic colloids differ in several respects and are closer in character to true solutions than are inorganic sols. They usually show the Tyndall effect, and visible particles may generally be seen through the ultra-microscope. They do not, as a rule, show any electrical character and are only precipitated by the addition of large quantities of electrolytes; but many of them acquire a charge in the presence of a small quantity of an acid or an alkali. They will then move in an electric field, and undergo precipitation by electrolytes like the colloidal suspensions (*i.e.* inorganic colloids).[1] Again, an organic colloid with water gives a mixture which is viscous and can become gelatinous (converted to a jelly, as with gelatine), whilst inorganic colloids (suspensions) are not viscous and do not gelatinise. Since also these organic colloids give colloidal solutions by mere contact with water, they are called *reversible colloids*, whereas the inorganic colloids are *irreversible*, since they cannot, after precipitation, be directly converted again into colloidal solutions by the same means.

Those colloidal solutions which are characterised by the definite electrical charge the disperse phase assumes, by their easy coagulation by electrolytes, their comparative rarity in Nature, and by the general necessity of first producing a certain degree of artificial subdivision before they can be formed, are sometimes termed solutions of *lyophobic* colloids. In general, the inorganic colloids are lyophobic. The other colloidal solutions, characterised by lack of definite electrical charge on the disperse phase, by a wide range of stability in the presence of electrolytes, by the frequency of their occurrence in Nature, and by the facility with which the disperse phase goes spontaneously into colloidal solution, are called solutions of *lyophyllic* colloids. In general, the organic colloids belong to this class.

Importance of Colloidal Chemistry.—A study of the colloidal state is of importance both from the theoretical and practical standpoint in chemistry. It has afforded convincing evidence of the reality of molecules and provided evidence of the correctness of the assumptions made in the Kinetic Theory. It is not very easy to differentiate sharply between solutions of crystalloids or true solutions, or colloidal solutions or suspensions, any difference being one of degree only. Thus, ordinary colloidal particles can be removed from solution by the Bechhold filters; colloids, both organic and inorganic, can be retained by parchment dialysers; whilst, finally, one may regard the molecules of a crystalloid such as sodium chloride or sucrose as filtered or retained by a membrane of copper ferrocyanide.

From the practical standpoint, the properties of colloids are of importance in connection with medicinal preparations, glass and earthenware manufacture, and dyeing processes; also in explaining the action of soaps[1] and the setting and hardening of cements, etc.

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[1] Hardy, *loc. cit.*

Specific Heats of Elements and Compounds.

Introductory.—The *heat capacity* (C) of a body is the amount of heat required to raise its temperature one degree centigrade. If the absorption of H units of heat raises the temperature from t_1° to t_2°, the *mean heat capacity* (C_m) of the body between t_1° and t_2° is given by

$$C_m = \frac{H}{t_2 - t_1}.$$

The *specific heat* (Q) of a substance is the heat capacity of the unit of mass, *i.e.* the amount of heat required to raise the temperature of one gram of the substance through one degree centigrade. When the specific heat of a substance at t° is referred to, it is understood to mean the heat absorbed by one gram between $(t - 0{\cdot}5)°$ and $(t + 0{\cdot}5)°$. This is an important point, since the specific heat of a substance varies with the temperature. The *mean specific heat* (Q_m) of a body of mass m over the range t_1° to t_2° is obviously given by the expression

$$Q_m = \frac{C_m}{m} = \frac{H}{m(t_2 - t_1)}.$$

The *atomic heat* of an element is the product of its atomic weight and specific heat. Similarly, the *molecular heat* of a substance, elementary or compound, is the product of its molecular weight and specific heat.

The C.G.S. *unit of heat*, in terms of which specific heats are expressed, is the *gram-calorie* (*cal.*), or the amount of heat required to raise the temperature of one gram of water through one degree centigrade. Sometimes the gram-calorie at 15° C. is chosen, sometimes that at 20° C., and at other times the mean gram-calorie between 0° C. and 100° C. is adopted. These units differ from one another, but only very slightly.

Since, then, water is the standard substance, it is important to determine, with the utmost accuracy, the variation of its specific heat with the temperature. This problem has been attacked by numerous investigators; the most trustworthy results are probably those of Callendar and Barnes,[2] and of Callendar.[3] According to the last-named investigator, the formula

$$Q = 0{\cdot}98536 + 0{\cdot}504/(t + 20) + 0{\cdot}0000084t + 0{\cdot}0000009t^2$$

satisfactorily represents the specific heat of water, in terms of the calorie at 20°, at all temperatures between 0° and 100°, and yields results in close agreement with those obtained by Callendar and Barnes.[4] These are given in the accompanying table. The unit employed is the calorie at 20°.[5]

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[1] See Spring, *Bull. Acad. roy. Belg.*, 1909, p. 187; *Rec. trav. chim.*, 1909, **28**, 424; *Bull. Soc. chim. Belg.*, 1910, **24**, 17; M'Bain and Martin, *Trans. Chem. Soc.*, 1914, **105**, 957.

[2] Callendar and Barnes, *Phil. Trans.*, 1902, A, **194**, 55, 149.

[3] Callendar, *Phil. Trans.*, 1912, A, **212**, 1; *Proc. Roy. Soc.*, 1912, A, **86**, 254.

[4] Callendar and Barnes, *loc. cit.*, and "Calorimetry" in *Encyclopædia Britannica*.

[5] For other investigations see Bartoli and Stracciati, *Beiblatter*, 1891, **15**, 761; 1893, **17**, 542, 638, 1038; *Boll. mens. dell' Acc. Gioenia*, 1891, **18**, April 26; Griffiths, *Phil. Mag.*, 1895, (v.), **40**, 431; Ludin, *Dissertation*, Zurich, 1895; Rowland, *Proc. Roy. Soc.*, 1897, **61**, 479; W. R. Bousfield and W. E. Bousfield, *Phil. Trans.*, 1911, A, **211**, 199.

SPECIFIC HEAT OF WATER.

t°.	Q.	t°.	Q.	t°.	Q.
0	1·0094	16	1·0009	40	0·9982
1	1·0085	17	1·0007	45	0·9984
2	1·0076	18	1·0004	50	0·9987
3	1·0068	19	1·0002	55	0·9993
4	1·0060	20	1·0000	60	1·0000
5	1·0051	21	0·9999	65	1·0008
6	1·0048	22	0·9997	70	1·0016
7	1·0042	23	0·9995	75	1·0024
8	1·0037	24	0·9994	80	1·0033
9	1·0032	25	0·9992	85	1·0043
10	1·0027	26	0·9991	90	1·0053
11	1·0023	27	0·9990	95	1·0063
12	1·0020	28	0·9989	100	1·0074
13	1·0017	29	0·9988		
14	1·0014	30	0·9987		
15	1·0011	35	0·9983		

Thus the gram-calorie at 15° is equal to 1·0011 gram-calories at 20°, and the mean gram-calorie between 0° and 100° is equal to 1·0016 gram-calories at 20°.

The heat imparted to a substance may be utilised in three ways:—

1. In increasing the kinetic energy of translation of the molecules, *i.e.* in raising the temperature (Q_t).
2. In performing work against external pressure consequent upon expansion (Q_p).
3. In overcoming the mutual attraction of the molecules (Q_a).

Hence

$$Q = Q_t + Q_p + Q_a.$$

The quantity Q_a depends upon several factors—such as dissociation, the breaking down of associated molecules, the overcoming of cohesive forces during change of state, etc., the thermal effects of which, being closely connected, are conveniently grouped together.

It is clear that Q will only remain constant with rise of temperature when Q_p and Q_a are very small. In such an event

$$Q = Q_t \text{ (approximately)},$$

and Q_t may be termed the *true specific heat*.

For solids and liquids Q_p is negligible owing to their comparatively small coefficients of expansion, and

$$Q = Q_t + Q_a.$$

According to Sohncke[1] Q_a is negligible for elements the molecules of which are monatomic, as, for example, most metals. For complex molecules, however, Q_a may be a very varying quantity, and the gradual fall of the specific heat of water until 40° C. is reached, and the subsequent rise in the same as that temperature is exceeded, may probably be explained in this way.

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[1] Sohncke, *Wied. Annalen*, 1898, 66 111.

As a general rule, for solids and liquids at temperatures above the ordinary, Q is approximately a linear function of the temperature. It may be represented over a limited range by an empirical formula of the type—

$$Q = a + \beta t + \gamma t^2,$$

where β is very small (in general) and γ is extremely small.[1] With lithium, aluminium, and one or two other metals the values of β are considerable. The variation in the specific heat of a metal with the temperature between 0° and 100° is for many purposes negligible.

In the accompanying table will be found the mean specific heats and atomic heats of the solid and liquid elements (over the temperature intervals given in the second column).

TABLE OF SPECIFIC AND ATOMIC HEATS OF THE ELEMENTS.[2]

Element.	Temperature Interval.	Mean Specific Heat.	Atomic Weight.	Mean Atomic Heat.
	° C.			
Aluminium[3]	16 to 100	0·2122	27·1	5·75
Antimony	0 to 100	0·0495	120·2	5·95
Arsenic (cryst.)	21 to 68	0·0830	75·0	6·23
,, (amorph.)	21 to 65	0·0758	75·0	5·70
Barium	−185 to 20	0·0680	137·4	9·34
Bismuth	9 to 102	0·0298	208·0	6·24
Boron (cryst.)[4]	0 to 100	0·2518	11·0	2·77
,, (amorph.)	0 to 100	0·3066	11·0	3·37
Bromine (solid)	−78 to −20	0·0843	79·9	6·73
,, (liquid)	13 to 45	0·1071	79·9	8·55
Cadmium	0 to 100	0·0548	102·4	5·63
Cæsium	0	0·0522	132·8	6·93
Calcium	0 to 100	0·1490	40·1	5·98
Carbon (wood charcoal)	0 to 99	0·1935	12·0	2·33
,, (graphite)[4]	19 to 1040	0·3100	12·0	3·72
,, (diamond)[4]	15 to 1040	0·3660	12·0	4·39
Cerium	0 to 100	0·0450	140·3	6·31
Chlorine (liquid)	0 to 24	0·2262	35·5	8·02
Chromium	22 to 51	0·1000	52·0	5·20
Cobalt	15 to 100	0·1030	59·0	6·08
Copper[3]	15 to 238	0·0951	63·6	6·05
Gallium (solid)	12 to 23	0·0790	69·9	5·52
Germanium	0 to 100	0·0737	72·5	5·34
Glucinum[4]	0 to 100	0·4246	9·1	3·87
Gold	0 to 100	0·0316	197·2	6·23
Indium	0 to 100	0·0570	114·8	6·54

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[1] See ...le, *Mém. couronnés Acad. roy. Belg.*, 1855, **27**, [i.], 1.
...ll Evans, *Physico-Chemical Tables*, vol. i. p. 183 (Griffin & Co., 1902), gives a
Bull. Soc. ch. ...o list of the specific heats of elements, and for further details of these the
957. ...red to his comprehensive work. See also Landolt-Bornstein, *Physikalisch-*
[2] Callendar a... Berlin, 3rd ed., 1913; *Physical and Chemical Constants*, by Kaye and
[3] Callendar, *Ph...* Co., 1911). T. W. Richards and F. G. Jackson (*Zeitsch. physikal.*
[4] Callendar and Ba... have determined the specific and atomic heats of many elements at
[5] For other investig... ...ve an excellent summary of earlier work. H. Schimpff (*Zeitsch.*
17, 542, 638, 1058; *Boll.* ...57) covers somewhat similar ground.
Mag., 1895, (v.), **40**, 431. Li... 1910, (iv.), **31**, 597.
1897, **61**, 479; W. R. Bousfield a...

[4] See p. 90.

TABLE OF SPECIFIC AND ATOMIC HEATS OF THE ELEMENTS—*continued.*

Element.	Temperature Interval.	Mean Specific Heat.	Atomic Weight.	Mean Atomic Heat.
	° C.			
Iodine (solid)	9 to 98	0·0541	126·9	6·86
Iridium	0 to 100	0 0323	193·1	6·24
Iron	20 to 100	0·1190	55·8	6·64
Lanthanum	0 to 100	0·0449	1[illegible]·0	6·24
Lead[1]	18 to 100	0·0310	207·1	6·41
Lithium	0 to 100	0·9102	6 9	6 28
Magnesium	18 to 99	0·2460	24·3	5·98
Manganese	14 to 97	0·1217	54·9	6·68
Mercury (solid)	–78 to –40	0·0319	200·6	6·40
,, (liquid)	20 to 50	0·0331	200·6	6·64
Molybdenum	15 to 91	0·0723	96·0	6·94
Nickel	18 to 100	0·1090	58·7	6·40
Nitrogen (liquid)	–208 to –196	0 4300	14·0	6·02
Osmium	18 to 98	0 0311	190·9	5·94
Oxygen (liquid)	-200 to –183	0·3170	16·0	5·55
Palladium	18 to 100	0 0590	106 7	6·30
Phosphorus (yellow)	13 to 36	0·2020	31·0	6·26
,, (red)	15 to 98	0·1698	31·0	5·26
Platinum	0 to 100	0·0323	195·2	6·31
Potassium[2]	0	0·1728	39·1	6·75
Rhodium	10 to 97	0·0580	102·9	5·97
Rubidium[2]	0	0 0802	85 45	6·85
Ruthenium	0 to 100	0·0611	101·7	6·21
Selenium (cryst.)	22 to 62	0·0840	79·2	6·65
,, (amorph	18 to 28	0 0953	79·2	7·55
Silicon (cryst.)[4]	129	0·1961	28·3	5·56
Silver[1]	17 to 507	0·0590	107·9	6·46
Sodium[3]	0	0·2822	23·0	6 51
Sulphur (rhombic)	17 to 45	0·1630	32·1	5·23
Tantalum	–185 to 20	0 0326	181·5	5·92
Tellurium (cryst.)	15 to 100	0 0483	127·5	6·16
Thallium	20 to 100	0 0326	204·0	6 65
Thorium	0 to 100	0·0276	232·4	6·41
Tin (cast)	0 to 100	0·0559	119 0	6·65
Titanium	0 to 100	0·1125	48·1	5·41
Tungsten	15 to 93	0·0340	184·0	6·26
Uranium	0 to 98	0·0280	238 5	6·68
Vanadium	0 to 100	0·1153	51·0	5·88
Zinc	20 to 100	0·0931	65·4	6 08
Zirconium	0 to 100	0·0660	90 6	5 98

Dulong and Petit's Law.—In 1819 Dulong and Petit[5] drew attention to the fact that the product of the atomic weight and specific heat for the majority of the solid elements then known was constant—in other words, that the atoms have the same capacity for heat. From the data in the preceding table (pp. 88 and 89) the general applicability of Dulong and Petit's Law will be apparent.

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[1] A. Magnus, *Ann. Physik*, 1910, (iv.), 31, 597.
[2] Rengade, *Compt. rend.*, 1913, 156, 1897.
[3] E. Griffiths, *Proc. Roy. Soc.*, 1914, A, 89, 1914.
[4] See p. 90.
[5] Dulong and Petit, *Ann. Chim. Phys.*, 1819, [ii.], 10, 395.

Leaving out of consideration those elements which are gaseous at ordinary temperatures, it will be observed that the atomic heats of the elements *do not vary greatly from the mean value* 6·4. There are, however, a few notable exceptions, namely, boron, carbon, glucinum, and silicon. In 1872 Weber[1] showed that the specific heats of boron, silicon, and carbon possess abnormally large temperature-coefficients, and that at high temperatures the atomic heats of these elements approximate to the mean value found for the other elements, although a sufficiently high temperature was never attained at which the atomic heats actually became 6·4. A few of his results are given in the following table:—

THE ATOMIC HEATS OF CARBON, SILICON, AND BORON AT DIFFERENT TEMPERATURES.

Diamond.			Graphite.			Silicon			Boron[2]		
Temp °C.	Specific Heat.	Atomic Heat	Temp °C.	Specific Heat.	Atomic Heat.	Temp. °C	Specific Heat.	Atomic Heat.	Temp. °C.	Specific Heat	Atomic Heat.
−50·5	0·064	0·76	−50·3	0·114	1·37	−39·8	0·136	3·81	−39·6	0·192	2·11
+10·7	0·113	1·35	+10·8	0·160	1·92	+21·6	0·170	4·75	+26·6	0·238	2·62
85·5	0·177	2·11	138·5	0·254	3·05	86·0	0·190	5·32	76·7	0·274	3·01
206	0·273	3·28	219	0·325	3·90	129	0·196	5·50	126	0·307	3·38
615	0·444	5·33	640	0·450	5·41	184	0·201	5·63	177	0·338	3·63
987	0·462	5·55	982	0·469	5·62	232	0·203	5·68	233	0·366	4·33

Weber therefore suggested that, for the purpose of applying Dulong and Petit's Law, the values for the specific heats of the elements should be taken at those temperatures at which they increase most slowly.

Thirteen years later, Humpidge[3] determined the specific heat of glucinum at various temperatures and showed that at 500° C. the value remained nearly constant. His results are embodied in the following table:—[4]

THE ATOMIC HEATS OF GLUCINUM AT DIFFERENT TEMPERATURES.

Temperatures. °C.	Specific Heat	Atomic Heat.
0	0·3756	3·42
100	0·4702	4·28
200	0·5420	4·93
300	0·5910	5·38
400	0·6172	5·61
500	0·6206	5·65

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[1] Weber, *Phil. Mag.*, 1872, [iv.], 49, 161, and 276. Compare Tilden, *Trans. Chem. Soc.*, 1905, 87, 551.

[2] This was really a boride of aluminium. See Vol. IV.

[3] Humpidge, *Proc. Roy. Soc.*, 1885, 38, 188; 1885, 39, 1.

[4] This table is condensed from Miss Freund, *The Study of Chemical Composition*, p. 3 (Camb. Univ. Press).

It accordingly appears that if the temperature at which the specific heats of these elements are taken is sufficiently high, carbon, silicon, boron, and glucinum may fall into line with the other elements, and conform to the Law of Dulong and Petit, although as yet the value 6·4 has not been attained for the atomic heats of any of them.

It may well be urged, however, that it is not fair to take the specific heats of these four elements at the highest attainable temperatures and compare them with those of the other elements at lower temperatures in order to make them fall into line with an empirical law such as the one now under discussion; especially since the results of the numerous researches show that the atomic heats of certain metals rise considerably above the mean value of 6·4 when the temperature is raised. This is well illustrated by the following table:—[1]

THE SPECIFIC AND ATOMIC HEATS OF DIFFERENT METALS AT VARYING TEMPERATURES.

Absolute Temperature.	Aluminium.		Nickel		Platinum.	
	Specific Heat.	Atomic Heat.	Specific Heat.	Atomic Heat.	Specific Heat.	Atomic Heat.
300°	0·2053	5 52	0·1054	6 14	0·0311	6·01
500	0 2384	6·41	0 1233	7·19	0 0344	6 64
700	0·2531	6 81	0 1301	7 58	0·0372	7·19
900	...	..	0 1338	7·80	0·0397	7·67
1500	...	...	.	...	0 0461	8 91

It would appear, therefore, that the wisest course is to adopt Tilden's suggestion, and compare the specific heats of the elements between 0° and 100° and treat as irreconcilable exceptions all elements that do not conform to the law under these conditions.

It is worthy of note that the atomic heats of the solid elements at constant volume (A_v) show more regularity than do the atomic heats at constant pressure (A_p). The former may be calculated by utilising the relationship—

$$A_p - A_v = T\beta^2V \qquad \text{(i.)}$$

in which T, V, α, and β denote the absolute temperature, atomic volume, and coefficients of compressibility and expansion respectively. For fifteen elements, the compressibilities of which have been measured by Richards,[2] the mean value for the atomic heat at constant volume is 5·9 at 20° C., and the average deviation only 0 09.[3] From the researches of Gruneisen[4] it appears that the preceding equation may be simplified to

$$A_v = A_p - k.T.Q_p^2 \qquad \text{(ii.)}$$

where k is the constant for the particular element.

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[1] This table is condensed from Tilden's lists, *Trans Chem Soc.*, 1905, 87. 555.

[2] Richards, *Carnegie Institution Publication*, 1907, No. 76.

[3] Lewis, *J. Amer. Chem. Soc.*, 1907, 29, 1165.

[4] Gruneisen, *Ann. Physik*, 1908, 26, 393; 1910, 33, 33, 65, 1239.

Specific Heats at Low Temperatures.—In general the differences noticed between the atomic heats become accentuated at temperatures below 0° C. Numerous experiments at low temperatures have been made by Behn,[1] Tilden,[2] Dewar,[3] Schimpff,[4] Richards and Jackson,[5] Dewar,[6] and particularly by Nernst and his collaborators,[7] who have measured specific heats at temperatures down to the boiling-point of hydrogen. As the temperature is lowered, the specific heats of the elements fall, rapidly at first, but afterwards more slowly, tending towards the limit zero at the absolute zero of temperature. The accompanying table contains some of the results that have been obtained :—

Silver.		Lead.		Copper.		Zinc.		Aluminium		Diamond.	
T abs.	Atomic Heat.	T abs.	Atomic Heat.	T abs.	Atomic Heat.	T abs.	Atomic Heat.	T abs.	Atomic Heat.	T abs.	Atomic Heat.
173°	5·46	202°	6·23	173°	4·98	173°	5·32	173°	4·54	262°	1·14
123	4·97	198	6·27	123	4·29	123	4·84	123	3·71	232	0·86
86	4·40	193	6·02	88	3·38	94	4·55	88·3	2·62	222	0·76
77	4·07	123	5·89	33·4	0·538	85	4·24	86·0	2·52	220	0·72
66	3·66	101	5·75	27·7	0·324	75	3·95	83·0	2·41	209	0·66
53·8	2·90	63	5·65	23·5	0·223	64	3·51	35·4	0·33	205	0·62
45·4	2·47	36·8	4·40	...	...	43·7	2·17	32·4	0·25	92	0·03
39·1	1·90	28·3	3·92	...	...	36·3	1·71	...	...	88	0·03
35·0	1·58	23·0	2·96	...	...	33·1	1·25	...	...	30	0·00

If the preceding values are represented graphically, it will be seen (fig. 48) that not only do they indicate that the specific heat Q of an element vanishes when the absolute zero is reached, but also that its rate of variation with the temperature, viz. dQ/dT, vanishes also.

According to the recent researches of Dewar, it appears that at 50° abs. the atomic heat of an element is a periodic function of its atomic weight.

Specific Heats and the Quantum Theory.—Specific heat measurements at low temperatures are of great interest in connection with Einstein's theory of specific heats. From kinetic considerations it was calculated by Richarz[8] that the atomic heat at constant volume of a monatomic solid element should be equal to 3R or 5·95 calories. But the kinetic theory does not account for the deviations from the Law of Dulong and Petit or for the great variation of specific heats with the temperature. Planck and Einstein[9] assume that a vibrating atom cannot take the energy continuously, but only *discontinuously*, in definite units (the so-called *energy quanta*), which are for each atom or vibrating system proportional to the frequency of vibration; *i.e.* the vibrating atom of matter takes up "atoms" of energy, so to speak.

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[1] Behn, *Ann. Physik*, 1898, **66**, 237.

[2] Tilden, *Phil. Trans.*, 1900, A, **194**, 233 ; 1903, A, **201**, 37.

[3] Dewar, *Proc. Roy. Soc.*, 1905, A, **76**, 325.

[4] Schimpff, *Zeitsch. physikal. Chem.*, 1910, **71**, 257.

[5] Richards and Jackson, *ibid.*, 1910, **70**, 414.

[6] Dewar, *Proc. Roy. Soc.*, 1913, A, **89**, 158.

[7] Nernst, Koref, and Lindemann, *Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 247 ; Nernst *ibid.*, 1910, p. 262 ; 1911, p. 306 ; *Ann. Physik*, 1911, (iv.), **36**, 395 ; Nernst and Lindemann, *Sitzungsber. K. Akad. Wiss. Berlin*, 1911, p. 494 ; Koref, *Ann. Physik*, 1911, (iv.) **35**, 49.

[8] Richarz, *Ann. Physik*, 1899, **67**, 702.

[9] Einstein, *Ann. Physik*, 1907, (iv.), **22**, 180 ; 1911, **35**, 659.

It may then be calculated that the atomic heat of a monatomic element, the atoms of which can only vibrate about mean positions, should be equal to

$$3Re^{\beta\nu/T}.(\beta\nu/T)^2.\left(e^{\beta\nu/T}-1\right)^{-2},$$

where R denotes the ordinary gas constant (1·985 cals.), T the absolute temperature, ν the frequency of vibration of the atom, and β denotes a universal constant ($4{\cdot}865 \times 10^{-11}$). According to this formula, the atomic heat of an element is nil at the absolute zero, when dA/dT likewise vanishes. With rise of temperature, the atomic heat increases slowly, then more rapidly, and finally it again slowly increases towards the limit 3R. It is possible to reproduce the results of specific heat measurements at low temperatures

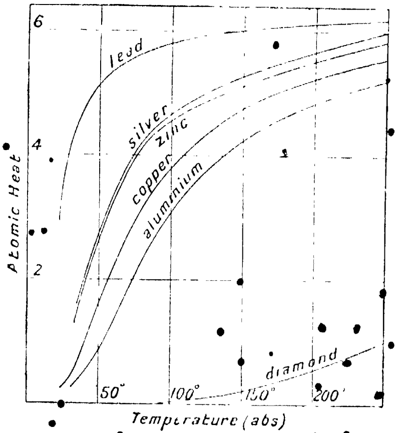

Fig. 48.—Variation of atomic heat with temperature.

with considerable accuracy by means of this formula; at extremely low temperatures, however, it gives results that are too small.

Einstein's formula refers to the atomic heat of a solid at *constant volume*. At very low temperatures this value differs inappreciably from the atomic heat at constant pressure, but at ordinary temperatures the difference is quite appreciable, and may be calculated by means of the above equation. Introducing Einstein's formula for A_v into the equation (ii.) of p. 91, and using the values of k obtained from Grüneisen's experimental data, it is found possible to reproduce the observed values of A_p with considerable accuracy for a number of metals by choosing suitable values of $\beta\nu$. The agreement at low temperatures is better if the modified equation

$$A_v = 1{\cdot}5R\left\{e^{\beta\nu/T}.(\beta\nu/T)^2.\left(e^{\beta\nu/T}-1\right)^{-2}+e^{\beta\nu/2T}.(\beta\nu/2T)^2\left(e^{\beta\nu/2T}-1\right)^{-2}\right\}$$

is adopted; this expression enables the specific heats of silver, lead, copper, and aluminium to be calculated with remarkable accuracy from the temperaure of liquid hydrogen to 550° abs., and with diamond the agreement holds up to 1100° abs.[1]

On the assumption that an element melts when the amplitude of vibraion of the atoms is equal to the distance between them, it can be calculated[2] hat the frequency ν is proportional to $\sqrt{T_s/mV^{\frac{2}{3}}}$, where T_s is the meltingoint, m the atomic weight, and V the atomic volume at the melting-point. rom this result and the preceding formula for the specific heat, it follows hat an element may be expected to deviate from the Law of Dulong and etit at ordinary temperatures if it has a low atomic weight and a high elting-point; on the other hand, an element of low melting-point and high tomic weight may be expected to follow the law, even at fairly low temperaures. The abnormal behaviour of boron, carbon, and silicon thus receives an explanation, and also the fact that the specific heat of lead only falls off slowly with the temperature.[3]

Determination of Atomic Weights.—For practical purposes it is best to assume, with Tilden, that Dulong and Petit's Law represents a rough, empirical rule, valid when the mean specific heats are determined between 0° and 100°, with three or four well-marked exceptions. In several cases the law has proved very useful as a means of fixing the atomic weights of several elements when their equivalent or combining weights have been known.

Uranium is a case in point. This element has a combining weight of 39·75; consequently its atomic weight is given by the expression

$$A = 39{\cdot}75 \times V,$$

where A is the atomic weight and V the valency. On account of the supposed resemblance of uranium to iron, the valency of uranium was taken as 3, and hence its atomic weight as $39{\cdot}75 \times 3 = 119{\cdot}25$. Mendeléeff,[4] however, placed the element in the sixth group of the periodical table along with chromium and sulphur. Hence an oxide of the formula UO_3 was to be expected, and therefore a valency of six. This meant doubling the atomic weight, which thereby became 238·5. The question was settled in 1882 by Zimmermann,[5] who found the specific heat of the element to be 0·027, from which, according to Dulong and Petit's Law, the approximate value of the atomic weight is given by the expression—

$$\frac{\text{Atomic heat}}{\text{Specific heat}} = \frac{6{\cdot}4}{0{\cdot}027} = 240.$$

Mendeléeff's views thus received confirmation.

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[1] Nernst and Lindemann, *Zeitsch. Elektrochem.*, 1911, **17**, 817.

[2] Lindemann, *Physikal. Zeitsch.*, 1910, **11**, 609.

[3] For further discussion of Einstein's formula and its application to compounds, see Nernst, *Zeitsch Electrochem.*, 1911, **17**, 265; Koenigsberger, *ibid.*, 1911, **17**, 289; Magnus and Lindemann, *ibid*, 1910, **16**, 269; and the references previously cited to Nernst and his collaborators. A new quantum theory, in which the quantum principle applies, not to the separate atoms of a body, but to the elastic waves which can be propagated through it, has been developed by Debye and by Born and von Kármán. It appears to be superior to Einstein's theory. According to the new theory, at temperatures not far removed from the absolute zero, the specific heat of an element is proportional to the cube of the absolute temperature. (See Debye, *Ann. Physik*, 1912, [iv.], **39**, 789; Born and von Kármán, *Physikal. Zeitsch.*, 1912, **13**, 297; 1913, **14**, 15; Thirring, *ibid.*, 1913, **14**, 867; Eucken, *Ber. deut. physikal. Ges.*, 1912, **15**, 571; Eucken and Schwers, *ibid.*, 1913, **15**, 578; Nernst and Lindemann, *Sitzungsber. K. Akad. Wiss. Berlin*, 1912, p. 1160; Nernst, *ibid.*, 1912, p. 1172.)

[4] Mendeléeff, *Annalen Supplement*,

[5] Zimmermann, *Ber.*, 1882, **15**, 847.

In a similar manner the atomic weights of indium, cerium, and lanthanum, have been determined.[1]

Specific Heats of Compounds.—In 1831 Neumann[2] extended Dulong and Petit's Law to certain groups of closely related compounds, as, for example, the carbonates of the alkaline earths, by drawing attention to the fact that these bodies exhibit the same molecular heats. This is well illustrated by the following table, in which the modern values for the specific heats and molecular weights of a number of sulphates are given:—

Substance.	Formula.	Temperature. °C	Specific Heat.	Molecular Weight.	Molecular Heat.
Calcium sulphate . .	$CaSO_4$	13–98	0·197	136·1	26·8
Barium sulphate . .	$BaSO_4$	10–98	0·113	233·4	26·4
Strontium sulphate . .	$SrSO_4$	21–99	0·143	184·7	26·3
Lead sulphate . .	$PbSO_4$	20–99	0·087	303·2	26·4

Regnault[3] extended Neumann's observations, and confirmed the law by more accurate determinations of the specific heats of metallic oxides, halides, sulphides, carbonates, sulphates, and nitrates.

Neumann's law, however, is only of limited application, inasmuch as it only applies to chemically related substances. Joule[4] and Woestyn[5] a few years later pointed out that the molecular heats of compounds are the sum of the atomic heats of the constituent atoms—a generalisation that enables us to connect all types of compounds together and is thus as universally applicable as Dulong and Petit's Law for the various elements. Since Kopp[6] did much to establish its truth, this generalisation is usually termed Kopp's Law, although it cannot be claimed that he was its originator.

It will be clear that Kopp's Law is tantamount to postulating that the atomic heats of the elements remain approximately the same whether the latter are free or combined; and that such is actually true in many cases is evident from the following table.—

Substance.	Formula.	Specific Heat.	Molecular Heat.
Silver chloride	$AgCl$	0·091	13·1 = 2 × 6·6
Cuprous chloride . . .	$CuCl$	0·138	13·6 = 2 × 6·8
Potassium chloride . . .	KCl	0·173	12·9 = 2 × 6·5
Barium chloride . . .	$BaCl_2$	0·090	18·8 = 3 × 6·3
Mercuric iodide . . .	HgI_2	6·012	19·1 = 3 × 6·4
Lead iodide	PbI_2	0·013	19·7 = 3 × 6·6

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[1] See Vol. IV.

[2] Neumann, *Pogg Annalen*, 1831, **23**, 1.

[3] Regnault, *Ann. Chim. Phys.*, 1841, [iii.], **1**, 129; *Pogg. Annalen*, 1841, **53**, 60 and 243.

[4] Joule, *Phil Mag.*, 1844, [iii.], **25**, 334.

[5] Woestyn, *Ann. Chim. Phys.*, 1848, [iii.], **23**, 295.

[6] Kopp, *Annalen Supplement*, 1864, **3**, 1, 289; *Proc. Roy. Soc.*, 1864, **13**, 229; ***Phil. Trans.***, 1865, **155**, 71. See also Thorpe, *Kopp Memorial Lecture*, delivered before the Chemical Society (London), February 20, 1893. Tilden, *loc. cit.*; Schubel, *Zeitsch. **anorg Chem.***, 1914, **87**, 81.

The following observations afford further arguments in favour of the truth of Kopp's Law:—

1. Bodies containing equal proportions of those elements which do not conform to Dulong and Petit's Law have approximately equal molecular heats. This is evident from a consideration of the different compounds of oxygen and sulphur shown in the table below, both oxygen and sulphur possessing abnormal atomic heats. The regularity here noticed is, of course, merely a special case of Neumann's Law.

Substance.	Formula.	Molecular Weight (O = 16).	Specific Heat.	Molecular Heat.
Copper oxide	CuO	79·6	0·142	11·4
Mercuric oxide	HgO	216·3	0·052	11·2
Nickel oxide	NiO	74·7	0·159	11 9
Iron sulphide	FeS	87·9	0·136	11·9
Lead sulphide	PbS	239·1	0·051	12·2
Mercuric sulphide	HgS	232·7	0·051	11·9

2. The values obtained for the atomic heats of abnormal elements are the same (approximately) whether deduced from the molecular heats of their compounds or calculated directly from the observed specific heats of the elements. Thus, in the table above, copper oxide (CuO) has a molecular heat of 11·4. Now, the specific heat of copper is 0·094 at temperatures ranging from 20° to 100° C., so that the atomic heat is $0·094 \times 63·6 = 6·0$, and the atomic heat of oxygen is in consequence $11·4 - 6·0 = 5·4$. The observed specific heat of liquid oxygen at $-190°$ C. is 0·347, whence its atomic heat is $0·347 \times 16 = 5·55$. This is a rather favourable example of the nature of the agreement observed.

Kopp's Law may be used to determine the atomic weight of an element the equivalent of which is known, irrespective of whether or not the pure element itself has been isolated. Thus, for example, suppose the atomic weight of mercury is required, analysis of mercuric chloride shows the equivalent of the metal to be 100·3, and, by applying one of the methods detailed in Chap. IV., it is found that the molecular weight of mercuric chloride is approximately 271·5. Evidently therefore the formula of the salt is Hg_nCl_2, and the problem is to find the value of n. A determination of the specific heat of mercuric chloride yields the value 0·069, and the molecular heat is therefore $0·069 \times 271·5 = 18·2$. From Kopp's Law, then, the number of atoms present in the molecule is $18·2/6·4 = 3$ (approximately); whence $n = 1$, the formula for mercuric chloride is $HgCl_2$, and the atomic weight of the metal $100·3 \times 2 = 200·6$.

Specific Heats of Gases.—Hitherto attention has been confined to the study of the specific heats of solids and liquids. With gaseous bodies new factors have to be considered, for in the equation

$$Q = Q_t + Q_p + Q_a$$

(*cf.* p. 87), Q_p may or may not be negligible according as the specific heat of the gas at constant volume or at constant pressure is determined. Of the two specific heats of a gas usually considered, the one measured at constant pressure exceeds that measured at constant volume by the thermal equivalent of the work required to overcome the resistance offered to the expansion of the gas. When a gram-molecule of a gas has its temperature raised through one degree centigrade at constant pressure it can be readily proved that the amount of work done during external expansion is represented by R, the constant in the gas equation—

$$PV = RT$$

(see p. 27). Furthermore, it can be shown that the work done in increasing the translational motion of the molecules of a gram-molecule of gas when heated through one degree centigrade is $\frac{3}{2}R$.

$$\text{Hence}\quad \frac{\text{Molecular heat at constant pressure}}{\text{Molecular heat at constant volume}} = \frac{Q_t + Q_p + Q_a}{Q_t + Q_a} = \frac{\frac{3}{2}R + R + Q_a}{\frac{3}{2}R + Q_a}.$$

Now, in the case of monatomic gases it may be assumed that the value for Q_a must be negligibly small, so that the following ratio for the specific heats is obtained :—

$$\frac{\text{Molecular heat at constant pressure}}{\text{Molecular heat at constant volume}} = \frac{\frac{3}{2}R + R}{\frac{3}{2}R} = 1{\cdot}67 = \gamma.$$

If, on the other hand, the gaseous molecules are diatomic or polyatomic, the value for Q_a may be expected to increase with the complexity of the molecule, and the value for γ to decrease in proportion. Hence, by determining γ for a given gas or vapour, it should be possible to obtain a clear indication as to whether its molecule is monatomic or complex. In order to do this, it is not necessary to actually make a determination of the two specific heats, for it was shown by Laplace that this may be deduced from a knowledge of the velocity of sound in the gas, by making use of the equation—

$$v = \sqrt{\gamma p/d} \quad \text{or} \quad \gamma = v^2 d/p,$$

where v is the velocity of sound, p the pressure, and d the density of the gas.

Kundt and Warburg[1] determined the velocity of sound in mercury vapour by means of the apparatus generally known as "Kundt's dust-tube,"[2] and deduced therefrom the value of 1·67 for γ, thus proving that mercury vapour consists of monatomic molecules. This result is in perfect harmony with the conclusions from the vapour density of mercury and its atomic weight as determined in other ways.

In the case of the inert gases of Group 0 in the periodic table it is impossible to make determinations of their atomic weights from a study of their compounds, as none are known to exist. Their molecular weights may be determined by the usual method for gases (see Chap. IV.), and the relationship between these magnitudes and the atomic weights may be derived from determinations of γ. The values obtained for γ always approximate closely to 1·67,[3] whence it is concluded that the molecules of the inert gases are monatomic.

In the case of diatomic gaseous molecules the value of γ is found by experiment to range from about 1·41 for the "permanent gases" to about 1·30 for those readily liquefiable. For triatomic molecules, *e.g.* H_2O, CO_2, etc., the values of γ are less than 1·3.

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[1] Kundt and Warburg, *Pogg. Annalen*, 1876, 157, 353.

[2] See this volume, Part II.

[3] See Part II. of this volume for references.

CHAPTER III.

SOLUBILITY, SOLUTION, AND SOME PROPERTIES OF SOLUTIONS.

Solubility and Solution.

It has been seen in the preceding chapter that it is impossible for two different gases in contact to remain in separate layers, however much their densities differ. The process of gaseous diffusion is, however, only a special case of what occurs when many substances, whether gaseous, liquid, or solid, are left in contact. Thus, if a limited quantity of salt be placed at the bottom of a vessel of water, it presently disappears as a solid, and can, by testing, be found distributed throughout the liquid. Few substances refuse to mix to some extent, however small. Carbon disulphide, for example, can dissolve very small quantities of water, and water of carbon disulphide; or, again, water can take up small quantities of silica, as well as of many other substances, such as silver chloride, which, for most practical purposes, are regarded as insoluble. Such admixture is termed *solution*, one of the substances being called the *solvent*; the other, usually the added substance, is called the *solute*. When a solid or a gas *dissolves* in a liquid, the latter is regarded as the solvent; a solid may be a solvent for a gas; and finally when two liquids are mixed, each may act as solvent or solute, as will be evident from a later section.

There are several points about the process of solution which may be noticed. If two substances which do not mix in every possible proportion are left in contact, and if at the end of a considerable time the added substance remains in excess, a saturated solution will have been formed. The rate at which this saturated state is reached depends on several factors, such as the state of subdivision of the solute, and the rate at which the solution formed diffuses away into the solvent. Agitation, which assists diffusion, causes solution to occur more quickly. The *solubility* of a substance in a given solvent is always a statement, in some form or other, of the relative proportions of solvent and solute that will yield a saturated solution at an assigned temperature and pressure. When saturation has been reached, whether by prolonged standing or by agitation, the solution will be homogeneous, having the same concentration in all parts.

A solution has already been defined[1] as a homogeneous mass of two or more substances, the composition of which can vary continuously between definite limits. This definition does not confine solutions to any particular state of matter, and it is possible to have solutions of gases in gases, of gases in solids, and of solids in solids, as well as of solutions of gases, liquids, and solids in liquid solvents. These different cases will now be discussed.

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[1] See Chap. I., p. 7.

Solubility of Gases in Gases.—From what has been said in connection with the diffusion of gases, it should be evident that there is no question of investigating the limits to which gases mix, for they are soluble in all proportions in one another.

When two or more gases are contained in the same vessel the pressure of the mixture may be determined by a simple rule known as *Dalton's Law*, according to which *the pressure exerted by a gaseous mixture is equal to the sum of the pressures which the constituents would exert if each occupied separately the volume of the mixture.*[1] The pressures which the constituents would exert separately are termed their *partial pressures* in the mixture. Denoting them by p_1, p_2, p_3, etc., and the total pressure of the gaseous mixture by P, then Dalton's Law may be simply stated thus:—

$$P = p_1 + p_2 + p_3 + \text{etc.}$$

In common with the other gas laws, Dalton's Law is only approximate, and at high pressures it breaks down. At moderate pressures, however, it holds with reasonable accuracy for vapours as well as gases, provided that the corresponding liquids are not miscible, as was shown by Regnault.[2] The law is commonly employed in deducing the volume, at any required temperature and pressure, of a dry gas from observations of its pressure, volume, and temperature when saturated with water or other vapour.

Leduc has shown that the following statement is more correct than Dalton's Law. "The volume occupied by a mixture of gases is equal to the sum of the volumes occupied by its constituents under the same conditions of temperature and pressure." For example, calculating from the densities of oxygen and "atmospheric nitrogen" at the same temperature and pressure, it is found that air contains 23·21 per cent. of oxygen, the experimental value being somewhere between 23·18 and 23·23 per cent. By using Dalton's Law as the basis of the calculation the value 23·33 is obtained.[3]

Solutions of Gases in Liquids.—The solubility of a gas in a liquid never takes place to an unlimited extent like that of one gas in another. The apparatus employed in the determination of gaseous solubility usually consists of the absorption vessel, a cylindrical glass funnel with taps at each end, and a gas-measuring apparatus from which a known volume of gas is transferred to the absorption vessel and in which, finally, the residual gas is measured.[4]

The results of solubility determinations can be expressed in one of two ways, either by the *absorption coefficient*, a term introduced by Bunsen, or by the *solubility*, or *coefficient of solubility*, a term due to Ostwald.

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[1] Dalton, *Mem. Manchester Phil. Soc.*, 1802, **5**, 543.

[2] Regnault, *Mém. de l'Acad.*, 1862, **26**, 722.

[3] Leduc, *Compt. rend.*, 1896, **123**, 805; 1898, **126**, 218, 413; *Ann. Chim. Phys.*, 1898, [vii.], **15**, 106; see also D. Berthelot and Sacerdote, *Compt. rend.*, 1899, **128**, 820; D. Berthelot, *ibid.*, 1899, **128**, 1159.

[4] For details of methods and apparatus see Bunsen, *Gasom. Methode* (Brunswick, 1877), 2nd edition; Timoféeff, *Zeitsch. physikal. Chem.*, 1890, **6**, 141; Winkler, *Ber.*, 1891, **24**, 89, 3602; *Zeitsch. physikal. Chem.*, 1892, **9**, 171; Bohr and Bock, *Ann. Physik*, 1891, **44**, 318; Steiner, *ibid.*, 1894, **52**, 275; Estreicher, *Zeitsch. physikal. Chem.*, 1899, **31**, 176; Braun, *ibid.*, 1900, **33**, 721; Just, *ibid.*, 1901, **37**, 342; Knopp, *ibid.*, 1904, **48**, 97; Geffcken, *ibid.*, 1904, **49**, 257; Christoff, *ibid.*, 1906, **55**, 622; Drucker and Moles, *ibid.*, 1911, **75**, 405; Fox, *Trans. Faraday Soc.*, 1909, **5**, 68; Usher, *Trans. Chem. Soc.*, 1910, **97**, 66.

The *absorption coefficient* is the volume of gas, reduced to 0° C. an 760 mm., which is dissolved at a particular temperature (that of experiment by unit volume of the liquid when the partial pressure of the gas is 760 mm In the following tables it is expressed by the symbol *a*.

The *solubility* or *coefficient of solubility* is defined as the volume of ga absorbed under the conditions of experiment by unit volume of liquid,[1] and is usually denoted by *l*. This quantity may also be stated as the ratio of the concentration of the gas in the gaseous space in a closed vessel to that in the saturated liquid below; for, by Henry's Law,[2] the volume dissolved is independent of the pressure.

The factors on which the solubility of a gas depends can be summarised under four heads, the solubility varying:—

(i.) With the nature of the gas.

The following table gives a comparison of the values of *a* for a number of gases at a temperature of 20°, the solvent being water:—

Gas.	*a*.	Gas.	*a*.
Helium	0·01386	Carbon dioxide	0·878
Hydrogen	0·01819	Chlorine	*l* = 2·260
Nitrogen	0·01542	Hydrogen sulphide	2·672
Oxygen	0·03102	Sulphur dioxide	*l* = 39·374
Argon	0·03790	Hydrogen chloride	*l* = 442·0
Carbon monoxide	0·02319	Ammonia	710·6

The neutral gases are soluble only to a small extent, whilst those with distinct acidic or basic properties dissolve readily, hydrogen chloride, ammonia, and methylamine, for example, being extremely soluble. A second point of interest lies in the fact that the gases exhibiting great solubility are generally the most easy to liquefy.

(ii.) With the nature of the solvent.

The influence of the solvent is shown very well by the following values obtained by Just[3] for the solubilities of nitrogen and carbon dioxide at 25° in various common solvents:—

Solvent.	Solubilities (*l*) of:	
	CO_2.	N_2.
[illegible]	0·0302	Immeasurably small
Water	0·8256	0·01634
Amyl alcohol	1·831	0·1225
Ethyl alcohol, 97%	2·706	
,, 99·8%	...	0·1432
Benzene	2·425	0·1159
Methyl alcohol	3·837	0·1415
Acetone	6·295	0·1460
Methyl acetate	6·491	...

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[1] The term *solubility* has also been defined as the volume of gas, reduced to 0° C. and 60 mm., which is dissolved by unit volume of the liquid when the total pressure (*i.e.* partial ressure of gas plus vapour pressure of solution) is equal to 760 mm. (L. W. Winkler, *Ber.*, 889, **22**, 1772). This definition is, of course, not equivalent to that given in the text.

[2] W. Henry, *Phil. Trans.*, 1803, 93, 29, 274.

[3] Just, *Zeitsch. physikal. Chem.*, 1901, 37, 342.

(iii.) With the temperature.

In nearly all cases the solubility decreases as the temperature rises. Th alteration of solubility is illustrated by the following table of absorptio coefficients of oxygen and nitrogen in water:—[1]

Temperature.	Oxygen.	Nitrogen.
0°	0·04890	0·02348
10°	0·03802	0·01857
20°	0·03102	0·01542
30°	0·02608	0·01340
50°	0·02090	0·01087
70°	0·01833	0·00976
90°	0·01723	0·00952
100°	0·01700	0·00947

Xenon, krypton, argon, neon, and helium differ from other gases i showing minima of solubility in water.[2]

When a solution of a gas in a liquid is heated in a vessel open to th atmosphere, the gas is gradually expelled, and, if its solubility is accuratel expressed by Henry's Law, is completely expelled when the boiling-point o the solvent is reached. Aqueous solutions of hydrogen chloride, bromide, an iodide in water do not behave in this manner. When a cold, saturate aqueous solution of one of these substances is heated, gas is evolved (with a little water); but even when the solution boils it still contains much dissolved gas, and eventually distils at a constant temperature unchanged i composition (see Vol. VIII.).

(iv.) With the pressure: *Henry's Law.*

The law connecting the effect of pressure with the solubility of a ga was discovered by Henry in 1803,[3] and states that the concentration of th solution is proportional to the pressure of the gas. If the pressure of a ga above a liquid solvent be doubled, the mass of gas absorbed will be doubled but by Boyle's Law the density of the gas is also doubled; hence the volum entering the solution remains constant. From this fact, as already stated, the volume of gas dissolved by a liquid is independent of the pressure. The very soluble gases, *e.g.* hydrogen chloride and ammonia, show deviations from Henry's Law.

If a mixture of gases be shaken with a solvent, the amount of each absorbed depends on two factors, namely, the solubility and the partial pressure (see p. 99) which each exerts in the gaseous mixture. The partial pressures of oxygen and nitrogen in air are in the ratio of their proportions by volume, but since the solubility of oxygen is greater than that of nitrogen, the gas expelled from water which has been saturated with air will be proportionately richer in oxygen. Winkler[4] found the following were the amounts of gas expelled from 1000 c.c. of water saturated with air at temperatures recorded below. In the normal atmosphere the mean percentage of oxygen is merely 20·9 to 21·0 by volume, save in tropical countries, where it may fall to 20·4 per cent. :—

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[1] L. W. Winkler, *Ber.*, 1891, 24, 3602.

[2] See Part II. of this volume; also Estreicher, *Zeitsch. physikal. Chem.*, 1899, 31, 176; Antropoff, *Proc. Roy. Soc.*, 1910, A, 83, 474.

[3] Henry, *Phil. Trans.*, 1803, 93, 29, 274.

[4] See Landolt-Bornstein, *Physikalisch-chemische Tabellen*, 1905, p. 605.

Temperature.	O_2.	N_2 and Inert Gases.	Total.	O_2 per Cent. by Volume.
° C.	c.c.	c.c.	c.c.	
0	10·19	18·99	29·18	34·81
5	8·91	16·17	25·68	34·69
10	7·87	14·97	22·84	34·47
20	6·36	12·32	18·68	34·03
25	5·78	11·30	17·08	33·82
30	5·26	10·38	15·64	33·60

Solutions of Liquids in Liquids.—Great variations are possible in the limits of solubility of liquid substances. Some liquids, such as sulphuric acid and water, are capable of mixing in all proportions over a considerable range of temperature. Zinc and cadmium, zinc and tin, lead and tin provide examples of the same nature among fused metals.[1]

When two liquids do not mix in all proportions, *they form two layers* after shaking together (provided the one in smaller amount is more than sufficient to saturate the other), each being a solution. Thus, ether and water form two layers, the upper one a solution of water in ether, the lower a solution of ether in water. The two layers are spoken of as *conjugate solutions*, for the reason that on sufficiently raising the temperature, if the solubility of each in the other increases as the temperature rises, or lowering it if the mutual solubility decreases with rise of temperature, a point is ultimately reached at which the composition of each layer is the same, and the two constituents then mix in all proportions. The temperature at which complete miscibility is reached is called the *critical solution temperature*. Zinc and bismuth in the liquid state mix in all proportions at and above a temperature of 650°, this being the critical solution temperature, and below this point separation into two layers occurs.[2]

The mutual solubilities of liquids have been very fully investigated with organic substances.[3]

Solutions of Solids in Liquids.—In no case will a solid dissolve to an unlimited extent in a liquid. The influence of various factors, such as the rise of temperature on the solubility, has therefore to be determined. The results are then expressed numerically, as grams or as gram-molecules of solid taken up by a fixed amount of solvent, and solubility curves, in which the solubilities are plotted against the temperature, may be drawn.

One or both of two methods may be followed in determining the solubility of easily or moderately soluble substances, namely, to agitate the solid and liquid in a vessel maintained at the temperature desired, or to heat the two substances to a higher temperature than required, and then to cool to the temperature of investigation. In either case excess of the solid must be present, not only to ensure saturation, but also to prevent supersaturation, and the same value of the solubility ought to ensue whichever method is adopted.[1]

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[1] Heycock and Neville, *Trans. Chem. Soc.*, 1897, 71, 383. See also this volume, p. 117.

[2] Heycock and Neville, *loc. cit.*; Wright, *Proc. Roy. Soc.*, 1892, 50, 372.

[3] See Findlay, *The Phase Rule*, 3rd edition (Longmans & Co., 1911).

For salts, such as silver chloride and barium sulphate, which are but slightly soluble in water, special methods have been adopted depending on the measurement of the specific conductivity of a saturated solution, or on a determination of the electro-motive force of a concentration cell containing the salt in solution.[2]

The former method, which has had considerable application, is based on the assumption that the particular solution, although saturated, is so dilute that the salt may be considered as completely split up into its ions. Now, according to Kohlrausch's Law, the equivalent conductivity (see p. 206) of a salt increases with dilution up to a point, and then remains constant. This limiting value (μ_∞) is made up of contributions by each ion, called the *ionic conductivities*, the latter having the same value in whatever compounds the ions occur, provided the conductivity considered is the limiting value. Expressed in symbols, $\mu_\infty = u + v$, for any binary electrolyte, where u and v are the ionic conductivities. Since u and v are constants derivable from any salts containing the ions separately, it is obviously possible to calculate μ_∞ for any salt containing ions for which u and v are known. Thus, for silver chloride, $AgCl$, the ionic conductivity of the Ag ion is the same, whether derived from measurements with silver nitrate, $AgNO_3$, or silver chlorate, $AgClO_3$; and the same is true for the Cl ion, whether obtained from hydrochloric acid itself or from any soluble chloride. By addition of the two values so obtained, the limiting equivalent conductivity of silver chloride is derived. The calculation of the solubility can now be made in the following way: Let C be the specific conductivity of a saturated solution of the substance in highly purified water and V (unknown) the volume of solution containing 1 gram equivalent of the salt. The equivalent conductivity $= C \times V$.

But if the salt is fully ionised, the equivalent conductivity measured is the limiting value, μ_∞.

Hence, $\mu_\infty = u_{Ag} + v_{Cl} = CV$, and since u and v are known, and C is measured in the experiment, V can be calculated.

The following table contains values obtained by this process at a temperature of 18°,[3] the solubility being expressed in terms of milligrams of salt per litre of solution:—

Substance.	Solubility.	Substance.	Solubility.	Substance.	Solubility.
BaF_2	1630	$AgBr$	0·107	$CaSO_4$	2040
SrF_2	117	AgI	0·0035	$PbSO_4$	41
CaF_2	16	$BaSO_4$	2·3	$PbCrO_4$	0·2
$AgCl$	1·6	$SrSO_4$	114	$CaC_2O_4.H_2O$	6·4

See also Bottger, *Zeitsch. physikal. Chem.*, 1903, 46, 521; 1906, 56, 83; Weigel, *ibid.*, 1907, 58, 293; Melcher, *J. Amer. Chem. Soc.*, 1910, 32, 50.

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[1] For details of methods see, for example, Ostwald and Luther, *Physiko chemische Messungen*, 3rd edition, Leipzig, 1910; Eyre, *B. A. Reports*, 1910.

[2] For an account of the latter method, see Findlay, *Practical Physical Chemistry*, p. 215 (Longmans, 1906).

[3] Kohlrausch, *Zeitsch. physikal. Chem.*, 1904, 50, 355.

Turning now to a general consideration of the results of solubility measurements, the subject may perhaps be best dealt with, firstly, in relation to the effect of temperature and the nature of the solute; secondly, to the influence of the solvent; and finally to the influence of pressure.

1. *The Effect of Temperature and Nature of the Solute.*—This is well illustrated by the various types of solubility curves shown in figs. 49 and 50, obtained with different substances in aqueous solution.

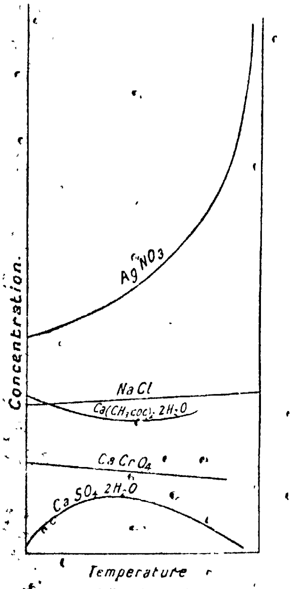

FIG. 49.—Solubility of salts in water.

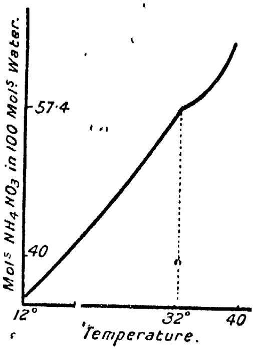

FIG. 50.—Solubility of ammoniur nitrate in water.

A differentiation can be made by classifying the curves according as they are continuous or exhibit sharp changes of direction.

A. *The curve is continuous.*

Several different types exist.

(*a*) The solubility increases uniformly with rise of temperature—rapidly as with silver nitrate, or slowly as with sodium chloride.

(*b*) The solubility decreases uniformly, as with calcium chromate.[1]

(*c*) The solubility increases to a maximum, and then diminishes, as witl gypsum, $CaSO_4.2H_2O$.[2]

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[1] Mylius and von Wrochem, *Ber.*, 1900, 33, 3689.

[2] Hulett and Allen, *J. Amer. Chem. Soc.*, 1902, **24**, 667; Van't Hoff, Armstrong Hinrichsen, Weigert, and Just, *Zeitsch. physikal. Chem.*, 1903, **45**, 257; Boyer-Guillon *Ann. Conservatoire Arts et Métiers*, 1900, [iii.], **2**; Tilden and Shenstone, *Phil* [illegible], 175, 23.

(iv) The solubility decreases to a minimum and then rises, as exemplified by calcium propionate[1] and by anhydrous sodium sulphate, the minimum in the latter case occurring at about 120° C.[2]

B. *The curve exhibits sharp breaks* Two possible causes, namely, a change of polymorphic form or a change of hydration,[3] will give rise to a sudden break in the curve. The former case is illustrated by ammonium nitrate, which is capable of existing in no fewer than four crystalline forms. Of these the β-rhombic passes into the α-rhombic variety at about 32° C.[4] At this temperature a break occurs in the solubility curve.[5]

The effect of change of degree of hydration in the case of those substances that can combine with water is shown in the solubility curve of sodium sulphate (fig. 51).[6] Below 32·8° C. the stable form of this salt crystallises with ten molecules of water, but above this temperature the anhydrous salt is stable. This transition-point is sharply marked by a break in the curve. So also the points of intersection in the solubility curve of ferric chloride (fig. 52) in water correspond with the appearances of new hydrated varieties

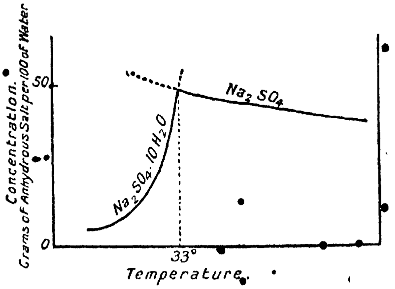

FIG. 51.—Solubility of sodium sulphate.

until at the last point of discontinuity there is transformation into the anhydrous substance.

From what has been said it will be evident that the determination of a transition-point (pp. 67-69) can be made by means of solubility measurements.

The solubility of a substance in water is closely connected with the heat evolved or absorbed when solution occurs. Many substances absorb heat on passing into solution, and in such cases the solubility increases with temperature. Salts capable of crystallising with water evolve heat when added in the anhydrous form, and it is found that the solubility of the anhydrous form usually decreases with rise of temperature.

Van't Hoff[7] gives the following rules, which, although applying in theory to the solution of a substance in a practically saturated solution, usually hold for ordinary solution: if a substance on solution gives out heat, rise of temperature will bring about a decrease in its solubility; if it absorbs heat, rise of temperature causes an increasing amount to pass into solution.[1]

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[1] Lumsden, *Trans. Chem. Soc.*, 1902, 81, 350.

[2] Tilden and Shenstone, *loc. cit.*

[3] *I.e.* an alteration in the solid phase in equilibrium with the solution.

[4] See p. 66, also see Vol. II.

[5] Müller and Kaufmann, *Zeitsch. physikal Chem.*, 1903, 42, 497.

[6] For a careful study of the changes in the solubility of sodium sulphate see de Coppet, *Ann. Chim. Phys.*, 1907, [viii.], 10, 457; H. Hartley, B. M. Jones, and G. A. Hutchinson, *Trans Chem. Soc.*, 1908, 93, 825.

[7] Van't Hoff, *Lectures on Theoretical and Physical Chemistry*, translated by Lehfeldt (Arnold), part i. pp. 37-9.

2. *The Influence of the Solvent.*—Several regularities of a general character have in recent years been brought to light connecting the extent of solubility with the nature of the solvent. Some of these hold both for solutions of solids and of liquids. It has been pointed out, for example, that miscibility of two substances will readily occur (i.) if both liquids, such as carbon disulphide and benzene, have simple molecules, (ii.) if both are associated, *e.g.* formamide, water and sulphuric acid; but the solubility of a non-associated substance in one that is associated is, as a rule, limited. Salts dissolve most freely in water, and it has been recently shown that in formamide this characteristic solvent power is reproduced very closely. Walden[2] also found that with a series of solvents the solubility of a salt was greater the more strongly associated the solvent.[3]

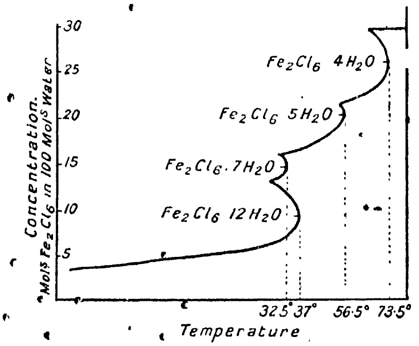

FIG. 52.—Solubility curve of ferric chloride in water.

Solubility is probably also connected with the dielectric constant or specific inductive capacity of the solvent. From a study of the mutual solubility of two liquids, Rothmund[4] suggested this relationship as existing, and, later, Walden[5] stated that when salts are dissolved by various liquids, the expression $\epsilon / \sqrt[3]{\mu}$ is approximately constant, where ϵ is the dielectric constant of the solvent and μ the percentage molecular solubility.[6]

Turner and Bissett[7] have shown, however, that the preceding relationship s by no means exact even in the case of solutes that are electrolytes, and breaks down completely when the solutes are non-electrolytes.

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[1] For a discussion of solubility from the point of view of the Phase Rule, see Findlay, *The Phase Rule and its Applications* (Longmans & Co., 1911), 3rd edition; see also Chap. V., p. 174.

[2] Walden, *Zeitsch. physikal. Chem.*, 1906, 55, 703.

[3] For discussion of the relation between solubility and association, see Crompton, *Trans. Chem. Soc.*, 1897, 71, 939; Turner, *Trans. Chem. Soc.*, 1911, 99, 902.

[4] Rothmund, *Zeitsch. physikal. Chem.*, 1898, 26, 433.

[5] Walden, *Zeitsch. physikal. Chem.*, 1908, 61, 633.

[6] *I.e.* $\mu = \frac{n \times 100}{N + n}$, n being the number of molecules of solute present in the saturated solution to N of the solvent.

[7] Turner and Bissett, *Trans. Chem. Soc.*, 1914, 105, 947.

3. *The Influence of Pressure.*—Sorby[1] concluded that a rise of pressure ncreases the solubility of those substances which dissolve in a liquid with contraction of volume, but that it decreases the solubility of such substances as dissolve in water with an increase in volume. This is in harmony with the Theorem of Le Chatelier (see p. 178) and has received further confirmation from the experiments of E. von Stackelberg,[2] the results of which are given in the following table:—

THE EFFECT OF PRESSURE ON SOLUBILITY.

Salt.	Change of Volume on Solution in Water.	Grams of Salt in one Gram of Solution at 18° C., at		
		1 Atmos. Pressure.	400 Atmos. Pressure.	500 Atmos. Pressure.
Sodium chloride . .	contraction	0·264	...	0·270
Ammonium chloride . . .	expansion	0·272	...	0·258
Alum	contraction	0·115	0·142	...

It was first indicated by Braun[3] that if the change of volume on solution and the thermal effect are known, the quantitative effect of alteration in pressure on the solubility may be readily calculated (see p. 183).

Solutions of Gases in Solids. Adsorption and Occlusion.—

Gases have the power both of diffusing through, and of being retained by, solid substances; and some of the phenomena observed are to be interpreted as due to the formation of a true solution analogous to that obtained when a gas dissolves in a liquid.

Hydrogen readily diffuses through metals, notably iron, platinum, and palladium. Deville and Troost[4] appear to have been the first to observe this in the case of red-hot iron and platinum, and in 1868 Cailletet[5] drew attention to the fact that hydrogen could pass through cold iron—an observation that was independently confirmed by Osborne Reynolds some six years later.[6] Winkelmann[7] found that the passage of hydrogen into an iron tube, forming the cathode in a cell, appeared to be independent of the pressure within the tube, and argued, therefore, that the hydrogen must diffuse in the form either of atoms or ions.

Palladium not only allows the diffusion of hydrogen, but absorbs and retains a large amount of hydrogen. Troost and Hautefeuille[1] believed that a compound Pd_2H was formed, but Wolf[2] suggests the formula PdH_2. The hydrogen is said to be *occluded* in the metal, the term *occlusion* signifying the existence of a solid solution, either of a gas in a solid or of one solid in another.

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[1] Sorby, *Proc. Roy. Soc.*, 1863, **12**, 538.

[2] E. von Stackelberg, *Zeitsch. physikal. Chem.*, 1896, **20**, 337.

[3] Braun, *Zeitsch. physikal. Chem.*, 1887, **1**, 259.

[4] Deville and Troost, *Compt. rend.*, 1863, **57**, 894.

[5] Cailletet, *Compt. rend.*, 1868, **66**, 847.

[6] Reynolds, paper read before the Manchester Literary and Philosophical Society, 24th February 1874.

[7] Winkelmann, *Ann. Physik.*, 1905, [iv.], **17**, 589. Compare M'Bain, *Phil. Mag.*, 1909, [vi.], **18**, 916; Hagenacker, *Zeitsch. physikal. Chem.*, 1909, **68**, 124; Sieverts and Langmuir, *J. Amer. Chem. Soc.*, 1912, **34**, 1310; 1915, **37**, 417; Langmuir and Mackay, *ibid.*, 1914, **36**, 1708.

Porous substances, such as charcoal, have the power of absorbing gases. Certain features of this absorbent action resemble the solution of gases in liquids. Thus, with charcoal, the extent of absorption depends, like that of a gas in a liquid :—

(1) On the nature of the gas, the most easily liquefied gases being absorbed to the greatest extent (see Vol. V.).

(2) On the temperature, a fact well illustrated by the following table of results found by Dewar :—[3]

Gas.	Volume absorbed by 1 c.c. of Charcoal at :	
	0° C.	- 185° C.
	c.c.	c.c.
Hydrogen	4	135
Nitrogen	15	155
Oxygen	18	230
Argon	12	175
Helium	2	15
Carbon monoxide . .	21	190

Obviously the amount absorbed decreases with rise of temperature.

According to Homfray,[4] Geddes,[5] and Titoff,[6] the absorption of a gas by charcoal is not regulated by Henry's Law, except, according to Titoff, for hydrogen between - 80° and + 80°. Equations have been deduced, however, to represent the absorption. Thus, for carbon dioxide in charcoal, Travers[7] found the value $C/\sqrt[3]{P}$ to be constant, where P is the pressure and C the concentration of the gas within the charcoal; whilst Hoitsema found the absorption of hydrogen in palladium to be represented by $C/\sqrt{P} = \text{const.}$

Now, Nernst has shown, and expressed the fact in his Partition Law[8] that Henry's Law holds also for solutions other than that of a gas in a liquid. As the absorption of a gas by a solid does not obey Henry's Law, the question naturally arose whether the absorption of a gas by charcoal was to be considered as a case of true solution, or due to a surface effect. Recently,

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[1] Troost and Hautefeuille, *Ann. Chim. Phys.*, 1874, [v.], 2, 279; *Compt. rend.*, 1874, 78, 686.

[2] Wolf, *Zeitsch. physikal. Chem.*, 1914, 87, 575; see Sieverts, *ibid.*, 1914, 88, 103, contrast Hoitsema, *ibid.*, 1895, 17, 1; Holt, Edgar, and Firth, *ibid.*, 1913, 82, 5; Halla, *ibid.*, 1914, 86, 496; Andrew and Holt, *Proc. Roy. Soc.*, 1913, A, 89, 170; also see Vol. IX.

[3] Dewar, *Compt. rend.*, 1904, 139, 261.

[4] Miss Homfray, *Proc. Roy. Soc.*, 1910, A, 84, 99.

[5] Geddes, *Ann. Physik*, 1909, [iv.], 29, 797.

[6] Titoff, *Zeitsch. physikal. Chem.*, 1910, 74, 641.

[7] Travers, *Proc. Roy. Soc.*, 1906, A, 78, 9.

[8] Nernst, *Zeitsch. physikal. Chem.*, 1891, 8, 110.

M'Bain[1] has been able to prove that the process occurring, as exemplified by the absorption of hydrogen by charcoal, is actually a combination of two processes—namely, a surface condensation termed *adsorption* which takes place rapidly, followed by a slow diffusion into the interior of the solid with the formation of a true solid solution. In view of the fact that the absorption of a gas by a solid is a combination of two processes, M'Bain has proposed to employ the non-committal term *sorption* when referring to the absorption as a whole, to call the diffusion of gas into the interior *absorption*, and to restrict the word *adsorption* to the first stage of sorption, namely, the surface condensation.[2]

Solutions of Solids in Solids. The term "solid solution" was applied by Van't Hoff to certain substances which separate in the crystalline state from liquid solutions on cooling, the crystals not being the pure solvent but a homogeneous mixture of solvent and solute—in short, solid solutions. A striking example of this came to light in the investigation by Beckmann and Stock[3] of the molecular weight of iodine in benzene solution. It was found that iodine always separated with the benzene in the solid state. Moreover, the ratio of the average concentration in the liquid to that in the solid was roughly constant; that is to say, Henry's Law held for the solid solution. If C_1 is the mean value—before and after freezing—of the concentration of iodine in the liquid, and C_2 the concentration in the crystals, each concentration being expressed in terms of iodine per 100 grams of benzene, then, for three different strengths of solution, the following figures were found:—

C_1.	C_2.	C_2/C_1.
3·39	1·279	0·377
2·587	0·925	0·358
0·9447	0·317	0·336

Apart from the cases arising from freezing-point measurements, however, miscibility in the solid state has been known for a considerable time. Until recently, it was believed that only isomorphous substances possess the power of crystallising out together, and, in turn, isomorphism was recognised by the power of mutual overgrowth and of forming mixed crystals (*i.e.* solid solutions), as, for example, in the case of the alums. It is now known, however, that overgrowths may occur with substances that are not isomorphous (see p. 72).

Miscibility in the solid state varies with the nature of the substances and the temperature. Retgers[4] defines six types of mixed crystals, according to the degree of solubility, this being dependent, according to him, on the degree of isomorphism or identity of crystalline form. The first type is that in which the two substances can mix in all proportions, as exemplified by zinc sulphate, $ZnSO_4.7H_2O$ and magnesium sulphate, $MgSO_4.7H_2O$, and is followed by other types in which the miscibility diminishes. In cases of limite solubility, two series of solid solutions are formed, each a solution of the on in the other, corresponding to conjugate liquid solutions. Thus, glucinu sulphate, $GlSO_4.4H_2O$, can take up glucinum selenate, $GlSeO_4.4H_2O$, unti the composite crystals reach a concentration at ordinary temperature of $7·33GlSO_4.4H_2O$, $GlSeO_4.4H_2O$, whilst the selenate can take up sul phate more extensively—until, in fact, a composition corresponding t $4GlSO_4.4H_2O$, $GlSeO_4.4H_2O$ is reached.

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[1] M'Bain, *Phil. Mag.*, 1909, [vi.], 18, 916; see also Firth, *Zeitsch. physikal. Chem.*, 1914, 86, 294.

[2] Cases of "sorption" analogous to those described in the text are observed when certain porous solids, *e.g.*, charcoal, are shaken up with solutions, a portion of the solute being "sorbed" by the solid. In the case of charcoal and solutions of iodine in various organic media it had previously been concluded by Davis that the process is one of "adsorption" followed by "absorption," just as in the "sorption" of gases (Davis, *Trans. Chem. Soc.*, 1907, 91, 1666; see also Adsorptive Power of Colloids, p. 84); contrast Schmidt-Walter, *Kolloid Zeitsch.*, 1914, 14, 242.

[3] Beckmann and Stock, *Zeitsch. physikal Chem.*, 1895, 17, 123.

[4] Retgers, *Zeitsch. physikal. Chem.*, 1890, 5, 461.

Modern research on the constitution of alloys has also brought to ligh many pairs of metals which are capable of forming solid solutions. Thus Ag and Au,[1] Co and Ni,[2] Sb and Bi[3] are examples of metals which can mi in all proportions in the solid state; whilst Cu and Ni,[4] Al and Zn[5], Au and Ni[6] are miscible only to a limited extent.[7]

The formation of solid solutions, or the occlusion of the reagent or othe salt by the precipitate, has also been noticed when precipitation occurs Thus, when $Fe(HO)_3$ is precipitated in the presence of certain proportion of manganese salts, manganese hydroxide is co-precipitated and the tw hydroxides appear to be in solid solution.[8] Possibly these phenomena occurring during precipitation may be shown by later investigation to be due partl to adsorption, analogous to the adsorption of hydrogen, iodine, and othe substances by charcoal.

Although the power of forming solid solutions has until recently bee connected with the isomorphous relations between the solids mixed, othe explanations have lately been advanced. Abegg[9] believes that the postulation of special crystallographic forces to explain the formation of double salt (a case of mixed crystal formation) is unnecessary and that the action o residual valencies can account for the phenomena observed Tammann[10] and Guertler,[11] in discussing the formation of solid solutions of the elements, both deny that isomorphism is the deciding factor. Tammann finds that th capability of forming solid solution depends more on the temperature o crystallisation than on the chemical analogies between the two substances whilst Guertler believes that the factors governing the formation of solid solutions are similar to those deciding the miscibility or otherwise of liquids Many pairs of elements are known to form extensive series of mixed crystal although the different members of a pair belong to different crystallographic systems.

Supersaturated Solutions.—When a solution of a solid in a liquid already saturated at a given temperature, is heated up with more of the solid until all the solid passes into solution, on cooling to the original temperatur the excess of the substance in solution is not always deposited, crystallisatio or precipitation being suspended. The solution obviously holds a greate quantity of substance than corresponds to the ordinary solubility and is sai to be *supersaturated*. Such solutions can readily be prepared by heating u sodium thiosulphate, sodium acetate, or sodium sulphate with water, an allowing to cool without agitation.

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[1] Roberts-Austen and Rose, *Proc. Roy. Soc.*, 1903, **71**, 161.

[2] Guertler and Tammann, *Zeitsch anorg. Chem.*, 1904, **42**, 353.

[3] Gautier, *Bull. Soc. d'Enc p. l'Ind. nationale*, 1896.

[4] Gautier, *Contribution à l'étude des alliages*, Paris, 1901.

[5] Shepherd, *J. Physical Chem.*, 1905, **9**, 504.

[6] Levin, *Zeitsch. anorg. Chem.*, 1905, **45**, 238.

[7] See, for a full discussion of these, E. F. Law, *Alloys* (Griffin & Co., 1909).

[8] See Korte, *Trans. Chem. Soc.*, 1905, **88**, 1503; Creighton, *Zeitsch. anorg. Chem.* 909, **63**, 53; Johnston and Adams, *J. Amer. Chem. Soc.*, 1911, **23**, 829.

[9] Abegg, *Zeitsch. anorg. Chem.*, 1904, **39**, 330.

[10] Tammann, *Zeitsch. Elektrochem.*, 1908, **14**, 789.

[11] Guertler, *Zeitsch physikal. Chem.*, 1910, **68**, 177.

Supersaturated solutions, however, are always liable to crystallis spontaneously, particularly on exposure to air. Löwell[1] was apparently th first to show, however, in the case of sodium sulphate, that crystallisatio was not induced by contact with air that had been previously passed throug water, sulphuric acid, caustic alkalies, glass wool, or even through a series o empty flasks. Fifteen years later Violette[2] and Gernez[3] independently thre a considerable light upon the subject by showing that the spontaneous crystallisation of supersaturated solutions of sodium sulphate in contact with air i due to the presence of minute crystals of the salt in suspension in the latter which serve as nuclei stimulating crystallisation. Hence by washing or filtering the air Löwell had removed these suspended nuclei, and in consequenc retarded crystallisation. Lecoq de Boisbaudran[5] showed, in the following year, that not only could minute crystals of the same substance serve a nuclei, but that crystals of isomorphous bodies yield precisely the same result; and it is now known that this property is shared by many substances that are not strictly isomorphous with the dissolved salt, provided their molecular volumes are closely similar.[6] Ostwald showed that nuclei weighing only 10^{-10} to 10^{-8} gram were usually quite sufficient to induce crystallisation of supersaturated solutions. Furthermore, it appears from numerous researches[7] that mere mechanical friction is sufficient to induce crystallisation, such crystallisation taking place in the complete absence of crystalline nuclei.

Supersaturated solutions of liquids in liquids have only been realised i a few cases,[8] but supersaturated solutions of gases in liquids are no uncommon. The addition of any powdered substance to such a solution however, will break down the supersaturation since the gases in the pore of the powder act as nuclei. Supersaturation of this kind differs from that considered above, inasmuch as the nuclei immediately escape from the liquid, whereby their influence is severely limited.

It will be clear that a supersaturated solution of a solid in a liquid cannot persist in the presence of the solid phase.

THE VAPOUR PRESSURE OF SOLUTIONS.

The Vapour Pressure of Liquid Mixtures at Constant Temperature.—As a general rule it may be said that when one liquid dissolves in a second, the pressure exerted by the mixtu of vapours is less than the sum of the independent vapour pressures. This is true whether the liquids are only partially miscible or are capable of being mixed in all proportions.[1]

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[1] Löwel, *Ann Chim. Phys.*, 1850, [iii.], 29, 62.

[2] Violette, *Compt. rend.*, 1865, 60, 831.

[3] Gernez, *Compt. rend.*, 1865, 60, 833 See also *ibid.*, 1865, 60, 1027, 1866, 63, 843.

[4] Traces of sodium salts are always present in our island atmosphere, and these yield sodium sulphite and sulphate by union with the oxides of sulphur produced during the combustion of coal, etc.

[5] Boisbaudran, *Ann. Chim Phys.*, 1866, [iv.], 9, 173; see also J. M. Thomson, *Zeitsch. Kryst. Min.*, 1881, 6, 94; Ostwald, *Lehrbuch*, vol. ii., part 2, p. 780

[6] See Isomorphism, pp. 70-74.

[7] A. H. Miers and his pupils, *Trans. Chem. Soc.*, 1906, 89, 413 1013; *Proc. Roy. Soc.*, 1907, A, 79, 322; B. M. Jones, *Trans. Chem. Soc.*, 1909, 95, 1672; Young, *J. Amer. Chem. Soc*, 1911, 33, 148; Young and Cross, *ibid.*, 1911, 33, 1375.

[8] H. S. Davis, *J. Amer. Chem. Soc*, 1916, 38, 1166.

On the other hand, if two liquids are insoluble one in the other, each exerts its own vapour tension independently of the other, and the total vapour pressure is the sum of the pressures exerted separately by the two vapours.

Dealing with liquids which can mix in all proportions, it has been found that the curve representing the relation of the vapour tension of the solution at constant temperature to the molecular concentration, follows one of the three general types shown in fig. 53.[2] The simplest is type I., lying evenly between the values for the separate constituents, and in the limit is a perfectly straight line, so that the vapour pressure could be calculated if the composition were known.[3] The more closely alike in chemical and physical behaviour the two liquids are, the more closely does the vapour tension curve of their mixtures conform to type I. Thus, ethyl chloride and ethyl bromide give a curve which is practically straight; methyl alcohol and water give a curve with slight convexity upwards—the curvature is more pronounced with ethyl alcohol and water; whilst propyl and the higher alcohols with water yield a curve with pronounced maximum values, corresponding to type II. There is thus a gradual passage from type I. to type II. as the difference in properties between the two liquids becomes greater. Liquid oxygen and nitrogen give a vapour tension curve which is nearly straight and that for oxygen and argon conforms also to type I.[4] Type III. has a minimum value, on the other hand, and represents the fact that the vapour tension of the mixture may e less than that of either constituent; e.g. formic acid and water.

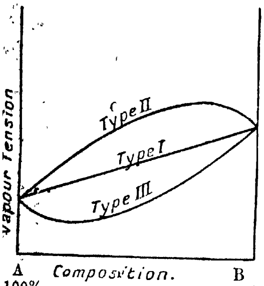

FIG. 53.

Distillation of Liquid Mixtures at Constant Pressure.—A olution boils when its total vapour pressure equals the external pressure. he composition of the vapour which passes over depends on the character f the liquids mixed. Thus, with liquids giving the curve of type II., the apour pressure of any mixture is always greater than that of the component i excess of what is required to form the mixture of maximum vapour pressure. Therefore, when such a solution is distilled, there is no separation into the two components; the liquid which comes over first as distillate is a mixture of the two components; and the residue continually approximates in composition to the component in excess. Thus, the boiling-points of water and of propyl alcohol respectively are 100° and 97·2° at 760 mm., but mixtures may distil at temperatures below 97·2°. For instance, the mixture containing 71·7 per cent. by weight of propyl alcohol corresponds with the maximum point on the vapour-pressure curve for 87·7°, and at that temperature its vapour pressure is 760 mm. Hence the mixture distils as a whole at 87·7° without change of temperature or composition. Any two substances giving a curve of type II., similarly give what is known as a constant boiling mixture or mixture of minimum boiling-point. Such mixtures were once thought to be compounds; but with alteration of the pressure the compositions of the distillate and residue were found to vary, thereby characterising the liquids as mere solutions.

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[1] See Regnault, *Compt. rend.*, 1854, **39**, 345, 397.
[2] Konovalow, *Wied. Annalen*, 1881, **14**, 34.
[3] See Zawidski, *Zeitsch. physikal. Chem.*, 1900, **35**, 129.
[4] Inglis, *Phil. Mag.*, 1906, [vi.], **11**, 640.

Liquid mixtures giving a vapour-pressure curve of type III. distil in such a way that the distillate first coming over is mainly the component in excess. The residue, therefore, continually approximates in composition to the mixture of lowest vapour pressure, and eventually there distils a second type of constant boiling mixture—namely, a mixture of maximum boiling-point.

Only with liquids giving a curve of the first type is a separation into the two components theoretically possible. The distillate always contains more of the higher vapour-pressure component and obviously the residue more of the lower.

Moissan and O'Farrelley[1] have shown that the binary alloys containing two of the metals Cu, Zn, Cd, Pb, and Sn, follow one or other of the three types of curves. Thus, Sn–Pb follow type I.; Cu–Pb, type II.; and Cu–Sn, type III. The last-named alloy upon distillation yields a constant boiling mixture containing 60 per cent. Sn.[2]

Fractional Distillation.—Even when the liquids have a vapour-pressure curve of type I., perfect separation is in practice impossible. If the distillate first obtained be redistilled or separated again into distillate and residue, the second distillate will be richer than the first in the more volatile component; and further treatment of the first residue in similar manner will leave a residue of the second component in a still purer state. By continuous repetition of these processes, separation may be made almost complete. Or, instead, the distillate may be collected in a number of separate receivers, in which case the first runnings will be very rich in one, and the residue rich in the second component. Such a process is known as *fractional distillation*.[3] If the mixed vapours be passed up a column, or through a still-head consisting of a series of bulbs, and thereby cooled, the higher boiling component is condensed more than the other, so that the vapour passing out of the head of the column consists mainly of the lower boiling liquid.[4]

In inorganic chemistry fractional distillation is employed to separate the various constituents of the atmosphere from liquid air.[5] It is also used as a method of purification. (See Chap. VII.)

The Vapour Tension of Dilute Solutions.—The preceding sections have been concerned with the vapour tensions of solutions of any strength, and it has been seen that whenever solution occurs the pressure of the mixed vapours is always less than the sum of the separate pressures. When the solute is non-volatile the vapour tension of the solution is always less than that of the pure solvent. The earliest investigations of the vapour tensions of solutions dealt with non-volatile solutes. Thus, von Babo[6] in 1848 discovered that the ratio p'/p, where p' and p are the vapour tensions of an aqueous solution and of water respectively, is independent of the temperature, and Wullner[1] found that the lowering of vapour tension produced by a non-volatile solute was proportional to the concentration. These regularities were further tested by various workers, but most thoroughly by Raoult,[2] who used a variety of solvents in addition to water, and many types of solute. He found von Babo's Law to be true, and, for solutions which were not strong, Wullner's Law also. Much more striking than these regularities was Raoult's discovery that the molecular lowering of vapour tension of any one solvent is the same for different substances. The laws regarding the vapour tension of dilute solutions may therefore be stated as follows:—

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[1] Moissan and O'Farrelley, *Compt. rend.*, 1904, 138, 1659.

[2] See also Groves and T. Turner, *Trans. Chem. Soc.*, 1912, 101, 585.

[3] The method by which the separation of two liquids from a mixture is effected bears a considerable resemblance to the method, explained in Vol. IV., by which solids are separated by fractional crystallisation.

[4] For a discussion of methods and apparatus for the separation of liquids by distillation, see Young, *Fractional Distillation* (Macmillan & Co., 1903).

[5] See this vol., Part II.; Vols. VI. and VII. for nitrogen and oxygen.

[6] von Babo, see Ostwald, *Lehrbuch*, i. 706.

1. The ratio of the vapour tension of the solution to that of the solvent is independent of temperature (von Babo's Law).

2. The lowering of vapour tension (for a non-volatile solute) is proportional to the concentration at constant temperature (Wüllner's Law).

3. Equimolecular quantities of different substances dissolved in a fixed quantity of the same solvent produce equal depressions of the vapour tension (Raoult's Law) provided the temperature remains constant.

The *molecular depression of vapour tension* is a constant, C, defined by the equation

$$C = \frac{p - p'}{p} \cdot \frac{M}{m},$$

where M is the molecular weight of the solute, m the amount of it per 100 grams of solvent, and p and p' the vapour tensions of the solvent and solution respectively.

Raoult found that the relative depression $\left(\frac{p - p'}{p}\right)$ is equal to the ratio of the number of molecules of solute (n) to the total number of molecules present in solution, *i.e.*,

$$\frac{p - p'}{p} = \frac{n}{N + n},$$

where N is the number of molecules of the solvent. For dilute solutions, this reduces to

$$\frac{p - p'}{p} = \frac{n}{N}$$

with sufficient accuracy. Owing to ionisation (see p. 211), acids, bases, and salts give abnormal values for the molecular depression and do not follow Wüllner's Law.

The Freezing-Points of Solutions.

More than one hundred and twenty years ago, Blagden[3] discovered that [illegible] freezing-point of a solution of a salt in water lies below that of pure [illegible] itself, the extent of the depression being proportional to the concentration of the salt present. Later workers[1] have studied this phenomenon in greater detail.

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[1] Wull[illegible]er, *Pogg. Annalen*, 1856, **103**, 529; 1858, **105**, 85; 1860, **110**, 564.

[2] Raoult, [illegible] *Compt. rend.*, 1886, **103**, 1125; 1887, **104**, 976 and 1430; 1888, **107**, 442; *Ann. Chim. Phys.*, 18[illegible]88, [vi.], **15**, 375; 1890, [vi.], **20**, 297; *Zeitsch. physikal. Chem.*, 1888, **2**, 353.

[3] Blagden, *Ph*[illegible]*il. Trans.*, 1788, **78**, 277.

Raoult's experiments on freezing-points were not confined to solutions of salts in water, but included investigations of other classes of substances dissolved in a variety of solvents. From his results the general conclusion may be drawn that within certain limits, to be considered below, the addition of any substance to a solvent brings about a lowering of the freezing-point of that solvent, the extent of the depression increasing with the amount of substance added. This statement, it may be noted, is only true so long as the substance which separates out on freezing is the pure solvent.

These facts may be studied by returning in the first place to a consideration of what occurs when a dilute solution of a salt—sodium chloride, for example—is cooled from 0° downwards. Freezing first occurs at a temperature below 0°, depending on the amount of salt added, and the solid which separates is pure ice. Hence, by this process, the salt solution left is more concentrated than the original one, and will have a still lower freezing-point. By continued cooling, then, the water continuously separates as ice, and the remaining solution becomes more and more concentrated until saturation is reached. Obviously, at this point, separation of ice must also be accompanied by a deposition of salt, and solvent and solute separate out side by side. Moreover, since the concentration of the solution is maintained at a constant value, the freezing-point must also remain constant during the separation of ice and salt together. Guthrie,[2] who investigated the continued action of cooling on a solution of sodium chloride, believed that the ice and salt separated together as a compound, to which he gave the name *cryohydrate*, since complete solidification occurred always at − 22° and the amount of salt present was 23·6 per cent. The separation of the components at constant temperature and in constant proportion, not as a compound but as a mixture, is to be expected, however, from what has been said above, and the phenomenon is in accordance with the requirements of the Phase Rule (see p. 174). Apart from this, the ice can be removed by washing with alcohol, the physical properties, such as specific volume,[3] are those of a mixture, and, finally, microscopic examination reveals the separate existence of the two components.

The cryohydric temperature, or temperature at which complete solidification occurs, is obviously the lowest temperature to which a solution of sodium chloride can be cooled. All salts dissolved in water behave similarly, the actual cryohydric point depending on the nature of the salt. The following substances may be quoted by way of illustration :—[4]

Substance.	Cryohydric Point.	Molecules of Water per Molecule of Salt.
NaCl	− 22 °C.	10·5
K_2SO_4	− 1·2	114·2
NH_4Cl	− 15	12·4
NH_4I	− 27·5	6·4

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[1] Rudorf, *Pogg Annalen*, 1861, **114**, 63 ; 1862, **116**, 55 ; 1871, **145**, 599. Coppet, *Ann. Chim. Phys.*, 1871, [iv.], **23**, 366 ; 1871, **25**, 502 ; and **26**, 98. Raoult, *ibid.*, 1883, [v.], **28**, 133 ; 1884, [vi.], **2**, 66, 115 ; 1886, [vi.], **8**, 289, 317.

[2] Guthrie, *Phil. Mag.*, 1875, [iv.], **49**, 1 ; 1884, [v.], **17**, 462.

[3] Offer, *Sitzungsber. K. Akad. Wiss. Wien*, 1880, **81**, ii. 1058.

[4] Bancroft, *The Phase Rule*, New York, 1897.

Instead of starting with a dilute solution of salt and concentrating it by removal of ice, we may proceed by continuously adding the salt in small quantities at a time, and making a determination of the freezing-point after each addition. In this way a freezing-point curve may be traced (fig. 54), plotting temperature of freezing against concentration. Starting from 0°, the lower limit of the curve will be reached when the solution is saturated and the cryohydric point is reached. This point must also lie on the solubility curve of the salt in water, so that the cryohydric point is the point of intersection of the freezing-point curve and the solubility curve.

The solubility curve may be regarded as a second freezing-point curve, for just as the original freezing-point curve represents the series of equilibria at different temperatures, between ice and the salt solution, so the solubility curve deals with the equilibria between the solid salt and the solution. On cooling, ice separates out along AB, and salt along CB. The curve CB may be likened, therefore, to the freezing-point curve of water dissolved in salt.

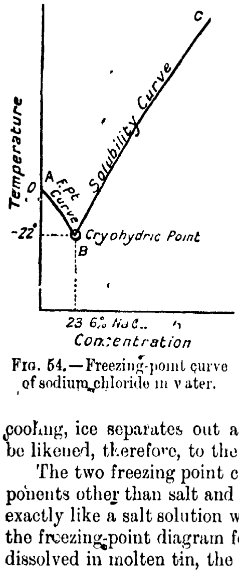

FIG. 54.—Freezing-point curve of sodium chloride in water.

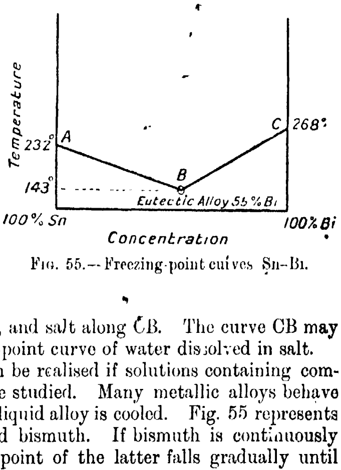

FIG. 55.—Freezing-point curves Sn–Bi.

The two freezing point curves can be realised if solutions containing components other than salt and water are studied. Many metallic alloys behave exactly like a salt solution when the liquid alloy is cooled. Fig. 55 represents the freezing-point diagram for tin and bismuth. If bismuth is continuously dissolved in molten tin, the freezing-point of the latter falls gradually until saturation is reached, and then deposition of the two metals at a constant temperature and in constant proportion occurs. This point cannot be termed the cryohydric point, since water is not involved; the general term *eutectic* is employed, the alloy which solidifies here having the *eutectic composition*. For bismuth and tin this eutectic composition is 45 per cent. Sn and 55 per cent. Bi, the eutectic temperature being 143°.[1] By starting with bismuth and adding tin, a second freezing-point curve is obtained ending in the eutectic point as before. Along AB, crystals of tin separate when the solution is cooled; along CB, crystals of bismuth.

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[1] Gautier, *Bull. Soc. d'Enc. Ind. Nationale*, 1896. See also Gulliver, *Alloys* (Griffin & Co., 2nd edition, 1913), where the properties and constitutions of alloys are fully discussed.

Fig. 56 represents the diagram for lead and silver mixtures. The eutectic temperature is 303°, and the eutectic alloy contains 4 per cent. Ag.[1]

It is obviously impossible to concentrate a solution of silver in lead beyond the 4 per cent. strength by removing lead as in Pattinson's process.[2]

The foregoing type of freezing-point curve is obtained only when the two components do not enter into chemical union and when they are incapable of forming solid solutions.[3]

When compounds are formed, for every compound produced, an additional branch is obtained containing a maximum point, if the compound has a definite melting-point under the prevailing pressure. Thus, with lead and magnesium[4] (fig. 57), magnesium separates out between A and B as cooling occurs; but at B the eutectic alloy deposited is found to consist, not of Mg and Pb, but of Mg and crystals of a new substance. If the eutectic alloy be remelted and more lead added, the freezing-point rises and the crystals separating on freezing are of neither Pb nor Mg, but the new substance. At the maximum point C, the compositions of the liquid and the crystals separating are the same, so that at this point also, solidification occurs as a whole and at constant temperature. Since we are dealing at C with only one crystalline form, the point C must represent the melting-point of the compound produced ($PbMg_2$). Further addition of lead lowers this melting-point, crystals of the compound continuing to separate as we pass from C to D, until a second eutectic is reached, consisting of the new compound

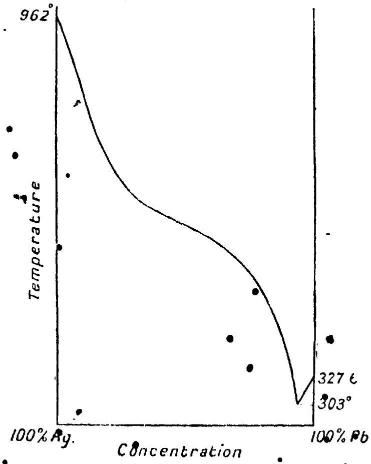

Fig. 56.—Freezing-point curve, Ag-Pb.

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[1] Heycock and Neville, *Phil. Trans.*, 1897, A, 189, 383.

[2] *Cf.* the Pattinson process for desilverising lead, Vols. II. and V.

[3] Two components which form solid solutions to a limited extent only also give a double branched freezing-point curve, but in this case the crystals separating out are not the pure solvent.

[4] Grube, *Zeitsch. anorg. Chem.*, 1905, 44, 117.

and lead. The curve ED is obtained either by remelting this second eutectic and continuing the addition of lead, or by starting out with lead and adding magnesium. The crystals separating along ED are those of lead.

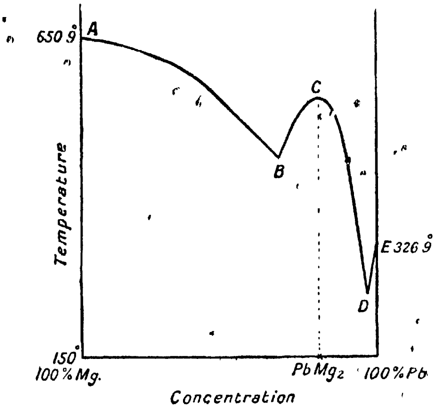

FIG. 57.—Freezing-point curve, Mg-Pb.

Whenever compounds can be frozen out from solution (and the phenomena are not complicated by the formation of solid solutions between the compound and one or other of the single components), an extra branch of the freezing-point curve and an extra eutectic point appear in the diagram for each compound formed. The maximum point on each added branch gives the melting-point and the composition of the compound. Thus with nitric acid and water[1] two compounds are formed, namely, $HNO_3.3H_2O$ and $HNO_3.H_2O$ (see fig. 58). Again, with ferric chloride and water, four hydrates, $Fe_2Cl_6.12H_2O$, $Fe_2Cl_6.7H_2O$, $Fe_2Cl_6.5H_2O$, and $Fe_2Cl_6.4H_2O$, are known, and each possesses a definite melting-point. These points are indicated by the maximum points in the curve (see p. 106).

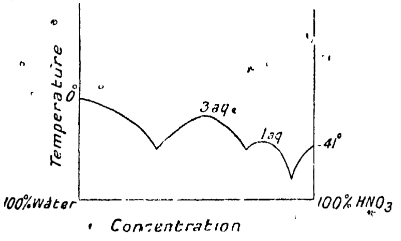

FIG. 58.—Freezing-point curve, HNO_3-water.

A study of the freezing-point curve is one of the most frequently used means of testing whether or not two substances, when mixed together in the liquid state, unite chemically.

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[1] Kuster and Kremann, *Zeitsch. anorg. Chem.*, 1904, 41, 1.

The third class of freezing-point curve represents the behaviour of liquid mixtures of substances which are soluble in one another both in the liquid and in the solid state, so that when freezing occurs, the crystals deposited contain both constituents, and are thus mixed crystals or solid solutions. If the two substances are soluble in one another in the solid state in all proportions, the freezing-point curve takes one of the three forms drawn in Fig. 59. Most pairs of inorganic substances follow type I., Bi–Sb,[1] Pt–Au,[2] Ag–Au,[3] and Co–Ni[4] providing examples.

Mixtures of mercuric bromide and mercuric iodide have a freezing-point curve of type III.,[5] which exhibits a minimum point. But little is known of

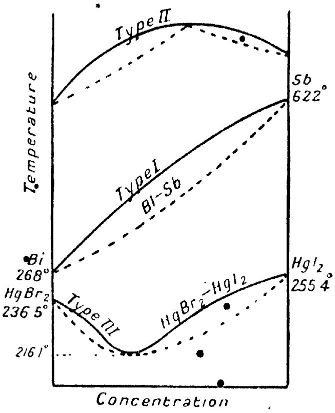

FIG. 59.

examples of type II., although mixtures of manganese and its carbide, Mn_3C, appear to follow this type.[6] It will be noticed that the three types of curve correspond with those which represent the vapour tensions of liquid mixtures.

In order to understand thoroughly the behaviour of mixtures of isomorphous substances, or those which form solid solutions, the melting-point curves of the solid substances separating must also be represented, for the composition of the solid phase depends on that of the liquid from which it separates (see p. 109). These melting-point curves are shown as broken lines in the figure. They coincide with the freezing-point curves at the maximum and minimum points.

If the solubility of the two substances in the solid state is limited, the freezing-point curve is not a continuous line, and the break is more pronounced the more limited the series of mixed crystals. Figs. 60 and 61 indicate the two types obtainable. There is an appreciable break in the

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[1] Gautier, *Bull. Soc. Enc. Ind. Nationale*, 1896.
[2] Erhard and Schertel, *Jahrbuch Berg- und Hutten-wesen*, Sachsen, p. 17.
[3] Roberts-Austen and Rose, *Proc. Roy. Soc.*, 1903, **71**, 161.
[4] Guertler and Tammann, *Zeitsch. anorg. Chem.*, 1904, **42**, 353.
[5] Reinders, *Zeitsch. physikal. Chem.*, 1900, **32**, 494.
[6] Ruff, *Ber.*, 1912, **45**, 3139.

Hg–Cd curve,[1] but it is only slight compared with that in the $TlNO_3$–KNO_3 curve.[2] In type B, lowering of freezing-point occurs with the separation of mixed crystals containing only a small percentage of the solute, until the solvent becomes saturated and a eutectic is produced. No eutectic is formed with a mixture belonging to type A, but a transition-point is observed. To each freezing-point curve there is a separate melting-point curve. The horizontal line in the diagram merely indicates the temperature at which there are in equilibrium the liquid solution and the two sets of mixed crystals.

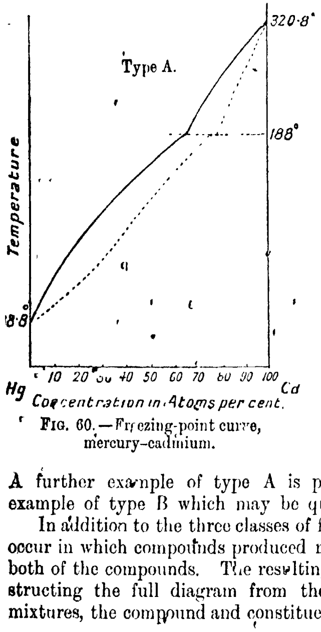

FIG. 60.—Freezing-point curve, mercury–cadmium.

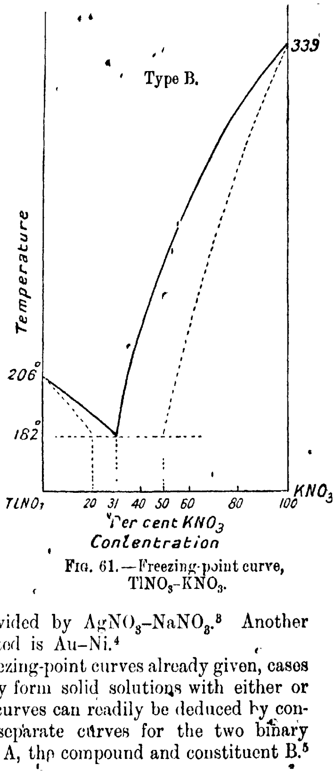

FIG. 61.—Freezing-point curve, $TlNO_3$–KNO_3.

A further example of type A is provided by $AgNO_3$–$NaNO_3$.[3] Another example of type B which may be quoted is Au–Ni.[4]

In addition to the three classes of freezing-point curves already given, cases occur in which compounds produced may form solid solutions with either or both of the compounds. The resulting curves can readily be deduced by constructing the full diagram from the separate curves for the two binary mixtures, the compound and constituent A, the compound and constituent B.[5]

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[1] Bijl, *Zeitsch. physikal. Chem.*, 1902. 41, 641.

[2] Van Eyk, *Zeitsch. physikal. Chem.*, 1899, 30, 430.

[3] Hissink, *Zeitsch. physikal. Chem.*, 1900, 32, 542.

[4] Levin, *Zeitsch. anorg. Chem.*, 1905, 45, 236.

[5] For a more complete account of freezing-point diagrams, see Findlay, *The Phase Rule*, 3rd edition (Longmans & Co., 1911); Goerens, *Introduction to Metallography*, translated by Ibbotson (Longmans & Co., 1908); Desch, *Metallography* (Longmans & Co., 1910); Desch, *Intermetallic Compounds* (Longmans & Co., 1914); Gulliver, *Alloys* (Griffin & Co., 2nd edition, 1913).

Purification by Fractional Crystallisation or Liquation.—Crystallisation as a means of separating two substances in a state of purity from a mixture is comparatively simple when each component, acting as the solvent, freezes out in the pure state; but when the substances form mixed crystals, separation can only be effected by a lengthy repetition of the process, as with fractional distillation, and there are certain cases in which no separation can be brought about. The process necessary will be understood by reference to fig. 62, which shows a portion of the freezing- and melting-point curves of mercuric bromide and iodide. Since the curves are temperature-concentration curves, it is obvious that the solid separating contains more of the bromide than the remaining liquid. At the temperatures t_1, t_2, and t_3, the concentrations of mercuric iodide in the crystals are represented by A, C, and E respectively; in the liquid, by B, D, and F. As the temperature falls from t_1 to t_3, both liquid and the deposited solid vary in composition. If, on the other hand, the solid separating at t_3 be isolated and heated, the temperature must be continuously raised before complete melting is obtained. Starting with crystals of composition E, and applying heat, there will be present at temperature t_2 a liquid of composition D and unmelted solid of composition C. If this still unmelted portion be isolated and heated to t_1, the solid now remaining is still richer in mercuric bromide. By a methodical repetition of these processes many times, on each fraction obtained, uniting portions that are similar in composition, it is possible to obtain finally a specimen of crystals which contains practically no iodide. A mixture of mercuric bromide and iodide can thus be separated into two portions, either bromide and the mixture of bromide and iodide of minimum freezing-point; or iodide, and the minimum freezing-point mixture, according as one starts with a mixture rich in bromide or iodide respectively. Only with a curve of type I. (*e.g.* Bi–Sb) can a separation into the two constituents be made. Thus, the process is strictly analogous to the distillation of liquid mixtures. If the composition of the mixture be that of the maximum or minimum point, where the freezing- and melting-point curves coincide, no separation can be made (unless the pressure be varied), the mixture behaving as a chemical compound of definite melting-point.

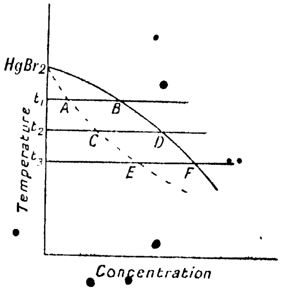

FIG. 62.—Fractional crystallisation of isomorphous mixtures.

The Freezing-Points of Dilute Solutions.—As indicated on p. 114, Blagden and subsequent workers found that the lowering of the freezing-point of a solution was proportional to the concentration of the solute. Raoult made a thorough test of this relationship,[1] using a variety of solvents and including many organic solutes, as well as, in aqueous solution, the salts which previous investigators had studied. Blagden's Law, that the lowering of freezing-point is proportional to the concentration, was found to be true, provided the solutions used were dilute; and it was further shown by Raoult that when the same solvent is used, equimolecular quantities of different solutes produce equal lowerings of freezing-point. If the gram-molecular weight, M, of the solute is dissolved in a fixed quantity of a solvent—for example, in 100 grams,—then the depression of freezing-point C° (termed the *molecular depression*) is constant whatever the solute. The actual value is obtained by the use of Blagden's Law. For, if *m* grams of solute dissolved in 100 grams of the solvent lower the freezing-point Δ°,

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[1] Raoult, *Compt. rend.*, 1882, 94, 1517; 95, 187 and 1030; *Ann. Chim. Phys.*, 1883, [v.], 28, 133; 1884, [vi.], 2, 66.

$$C : \Delta = M : m,$$

or,

$$C = \frac{\Delta M}{m}.$$

Conversely, having once fixed the value of C, the previously unknown molecular weight of a solute can be found.

It is now usual in defining C to make the fixed amount of solvent either 1 gram or 1000 grams, when C is either one hundred times greater or ten times smaller than in the above case.

Electrolytes depart from the laws of dilute solution enunciated in this section, just as they do in the case of the vapour-tension laws.

OSMOTIC PRESSURE.

When a substance passes into solution, it becomes uniformly distributed throughout the solvent, and in various ways its behaviour in this condition resembles that of a gas.

That a close analogy exists between the gaseous and the dissolved states is evident from a consideration of the process of diffusion in the two cases. A given quantity of a gas will expand to fill any space into which it is introduced, whether the space had previously been evacuated or contains some other gas. If a gas is present, the rate at which the added gas distributes itself is considerably retarded. The diffusion or expansion may occur even against gravitation, as when a heavy gas, or vapour (*e.g.* bromine), is introduced at the bottom of a cylindrical vessel. Like a gas, a substance in solution distributes itself throughout the whole volume of solvent. If a beaker of concentrated copper sulphate solution is placed in a large trough and the latter carefully filled with water, the salt gradually diffuses in all directions until the solution is of uniform concentration throughout. The rate of diffusion is very much slower than that of a gas, owing to the great resistance to movement encountered, but in other respects the two processes are essentially alike. Since the particles possess mass and velocity, there must in each case be some driving force or pressure, which, in the one case gives rise to gas pressure, and in the other (*i.e.* in solution) to *osmotic pressure.*

Gas pressure is readily measured at the surface or envelope which isolates the gas, and is due to the bombardment of the surface by the molecules. Although it is easy to measure total gas pressure, it is not easy to determine the pressure set up by a single gas present in a mixture. The measurement is possible if the pressure due to one gas can be eliminated by bringing it to some fixed value, for example, atmospheric pressure. To this end it is necessary for the containing vessel to be constructed of some material which exerts a selective action, allowing one gas to pass through it but not the other. The possibility of determining the pressure of nitrogen in a mixture of this gas with hydrogen has been demonstrated by Ramsay. A palladium tube containing the mixture was closed by a manometer an surrounded by an atmosphere of hydrogen at 280°, at which temperatur hydrogen diffuses rapidly through the metal, whereas nitrogen is quite unabl to do so Hydrogen therefore passed in until its partial pressure within wa equal to the pressure without—namely, atmospheric. The total pressure now registered exceeded one atmosphere, the excess being due to the nitrogen.

In a similar manner, the osmotic pressure of a substance in liquid solutio can be measured if the action of the solvent molecules can be eliminated For this purpose, some semi-permeable partition—that is, one permeable t the solvent but impermeable to the solute—is required. The selective actio of such partitions as are available appears to be due to the power of the partition to dissolve one of the constituents, which, in this way, finds a passage through from one side to the other.[2]

The surfaces of separation originally used in the study of osmosis were o animal membrane. Traube[3] first suggested the use of membranes composed of substances, such as copper ferrocyanide, which are precipitated in the gelatinous form.[4] Of the various precipitation membranes tested, this one has proved most useful. Pfeffer,[5] who made the first accurate measurements of osmotic pressure, deposited the precipitate within the pores of a cylindrical, unglazed, earthenware cell, thus providing a framework whereby the deposited membrane was greatly strengthened. The cells were thoroughly saturated with water to remove air, then filled with a 3 per cent. solution o potassium ferrocyanide and allowed to stand in a solution of copper sulphate of the same strength for some days. The methods of precipitation have been improved by later workers, and include an electrolytic process in which copper sulphate and a platinum electrode are placed within the cell and potassium ferrocyanide solution and a copper electrode surrounding the cell, the solutions both being fifth or tenth normal. On the passage of a current, a membrane is formed halfway between the inner and outer walls, which can be made strong enough to withstand a pressure of over thirty atmospheres.[6]

If a cell such as has been described is filled with a salt solution, closed by a stopper through which a straight tube passes and then immersed in water, the latter enters the cell and the solution rises up the tube, at first at a rate appreciable within a few minutes, later more slowly, until a maximum height is attained. The entrance of water is due to the tendency of the solute to diffuse under the action of osmotic pressure; and since the salt cannot pass through the membrane, water passes into the cell from without until equilibrium is attained, the height of solution in the tube above the water outside measuring the osmotic pressure. Owing to dilution, through

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[1] Ramsay, *Phil. Mag.*, 1894, [v.], 38, 206.

[2] See Nernst, *Zeitsch. physikal. Chem.*, 1890, 6, 38; Raoult, *ibid.*, 1895, **17**, **737**; Tammann, *ibid.*, 1897, **22**, 490; Flusin, *Compt. rend.*, 1896, **126**, 1497; 1900, **131**, 1308; Crum Brown, *Proc. Roy. Soc. Edin.*, 1899, **22**, 439, for an account of other theories which attempt to account for osmosis.

[3] Traube, *Archiv Anatomie und Physiologie*, 1867, p. 87.

[4] For other precipitation membranes, see Morse, *Amer. Chem. J.*, 1903, **29**, **173**.

[5] Pfeffer, *Osmotische Untersuchungen*, Leipzig, 1877.

[6] For various methods of preparing osmotic pressure cells, see Adie, *Trans Chem. Soc.*, 1891, **59**, 344; Morse and Horn, *Amer. Chem J.*, 1901, **26**, 80; Morse and Frazer, *ibid.*, 1902, **28**, 1; Morse and others, *ibid.*, 1911, **45**, 91, 383, 517; Berkeley and Hartley, *Phil. Trans.*, 1906, **A**, **206**, 481; J. H. Poynting and J. J. Thomson, *Properties of Matte* (Griffin & Co., 5th edition, 1909).

the entrance of water, the osmotic pressure thus registered is not that of the original solution, and to prevent the entrance of anything more than a trace of water, Pfeffer's later measurements were made with a closed air manometer of capillary tubing containing an index of mercury, the pressure being measured by the compression of the air.

The laws of osmotic pressure have been deduced mainly by a careful study of solutions of cane sugar (sucrose). Pfeffer found that the osmotic pressure of such a solution is proportional to the concentration, as is indicated by the following results for a temperature of 13·7° C.:—

Percentage Concentration.	Osmotic Pressure in Atmospheres.
1	0·691
2	1·337
3	2·739
4	4·046

Further, it increases with rise of temperature. The following are Pfeffer's data for a 1 per cent. solution of sucrose:—

Temperature.	Osmotic Pressure in Atmospheres.	Temperature.	Osmotic Pressure in Atmospheres.
°C.		°C.	
6·8	0·664	22·0	0·721
13·7	0·691	32·0	0·716
14·2	0·671	36·0	0·746
15·5	0·684		

It was discovered by Van't Hoff[1] that, despite the irregularities in the above figures, Pfeffer's results give considerable support to the theory that the laws of osmotic pressure for dilute solutions correspond exactly with the gas laws. The temperature coefficient of osmotic pressure is approximately the same as that of gaseous pressure. Hence osmotic pressure (P) is proportional to the absolute temperature (T), or $P \propto T$. Since also the osmotic pressure is proportional to the concentration, it varies inversely as the volume (V) of the solution, *i.e.* $P \propto 1/V$. Hence, when temperature and concentration both vary, $P \propto T/V$, or

$$PV = R'T,$$

where R' is a constant. For a 1 per cent. solution of sucrose at 6·8° C., the osmotic pressure is 0·664 atmos., or $0·664 \times 76 \times 13·6 \times 981$ dynes per sq. cm., and V, the volume which contains 1 gram-molecule (342 grams) of sucrose, is 342×100 c.c. Further, $T = 273 + 6·8$. Hence,

$$R' = PV/T = \frac{0·664 \times 76 \times 13·6 \times 981 \times 34200}{(273 + 6·8)}$$
$$\doteq 8·23 \times 10^7 \text{ C.G.S. units.}$$

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[1] Van't Hoff, *Zeitsch. physikal. Chem.*, 1887, 1, 481; *Phil. Mag.*, 1888, [v.], 26, 81.

This value is in such excellent agreement with that of R in the gas equation (p. 27) as to quite justify Van't Hoff's statement that *the osmotic pressure of a substance in dilute solution is equal to the pressure that it would exert if it were converted into a gas at the same temperature as, and made to occupy the same volume as, that of the solution.* In the main, this statement has been fully confirmed by later workers.[1]

Since Pfeffer carried out his measurements, the osmotic pressures of aqueous solutions of sucrose have been the subject of numerous series of experiments by Morse and others, pressures of 28 atmospheres having been measured with accuracy.[2] As a result it has been found that even when solutions of only moderate concentration are examined, the osmotic pressures observed differ considerably from the values that would be expected if Van't Hoff's Law held good. Morse and Frazer[3] have proposed the following modification of Van't Hoff's Law, as being more accurate than the original statement: The osmotic pressure is that which the substance would exert if converted into a (perfect) gas and the volume reduced to that of the *solvent* in the pure state. Accordingly, Morse and his co-workers always prepared their solutions so as to be 0 1, 0·2, 0·3 . . . times weight-normal in concentration, a weight-normal solution containing one gram-equivalent of reagent per 1000 grams of solvent. The following data for sucrose at 20° will serve to illustate the superiority of Morse and Frazer's statement to that of Van't Hoff when other than dilute solutions are considered (pressures are given in atmospheres):—

Weight-Normal Concentration.	Osmotic Pressure observed.	Calculated Van't Hoff.	Osmotic Pressure, Morse and Frazer	Weight-Normal Concentration	Osmotic Pressure observed	Calculated Van't Hoff.	Osmotic Pressure, Morse and Frazer.
0·1	2·59	2·34	2·39	0·6	15·39	12·72	14·34
0 2	5·06	1·59	4·78	0·7	18·13	14·58	16·73
0·3	7·61	6 74	7·17	0·8	20 91	16·36	19·12
0·4	10·14	8 82	9·56	0·9	23·72	18·08	21 51
0·5	12·75	10 81	11·95	1·0	26·61	19·[illegible]	23·90

Morse and Frazer's rule, however, is only approximately true, and breaks down completely when applied to the high osmotic pressures measured by Berkeley and Hartley.[4]

The effect of temperature upon the osmotic pressure has been shown by Morse and his co-workers to resemble that observed in the case of gaseous pressure, if allowance is made for the combination occurring between water and sucrose.

The osmotic pressure of a dilute solution of a *salt* is not proportional to the concentration, and on comparison with a non electrolyte a molecular quantity of a salt always exerts much the higher osmotic pressure. As an example, the data for aqueous potassium ferrocyanide may be quoted :—[1]

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[1] For a short account of Van't Hoff's theory and its limitations, see Chap VI.

[2] Morse and others, *Amer. Chem. J.*, 1905, **34**, 1; 1906, **36**, 1, 39; 1907, **37**, 324, 425, 558; **38**, 175; 1908, **39**, 667; **40**, 1, 194, 266, 325; 1909, **41**, 1, 92, 257; 1911, **45**, 91, 237, 383, 517, 554; 1912, **48**, 29 Pressures as high as 134 atmos. have been measured by the Earl of Berkeley and E. G. J. Hartley; see Berkeley and Hartley, *Phil. Trans.*, 1906, **A**, **206**, 481; 1908, **A**, **209**, 177; Berkeley, Hartley, and Stephenson, *ibid.*, 1909: **A**, **209**, 319.

[3] Morse and Frazer, *Amer. Chem. J.*, 1905, **34**, 1.

[4] See Lewis, *J. Amer. Chem. Soc.*, 1908, **30**, 668.

Grams $K_4Fe(CN)_6$ per 100gms. water	Observed Osmotic Pressure (Atmospheres).	Calculated Osmotic Pressure (Atmospheres).
13·580	19·25	7·95
8·897	13·72	5·29
5·631	9·19	3·39
3·035	5·41	1·84
1·518	2·93	0·93

For binary salts, such as sodium chloride, dilute solutions have an osmotic pressure of approximately twice the calculated value.[2] These "abnormal" values were first explained by Arrhenius on the assumption of ionisation (see p. 212).

Indirect Methods of Measuring Osmotic Pressure.—The osmotic pressures of different solutions may also be determined by comparison methods. The contents of plant cells are enclosed in semi-permeable membranes, and if the cells are placed in strong salt solutions the protoplasmic contents shrink away from the cell walls, which latter do not alter their shape. If the cells are now placed in pure water, the protoplasm swells out again and completely fills the cells. From this it is clear that if the osmotic pressure of the solution is greater than that of the cell sap, the protoplasm contracts—that is, *plasmolysis* occurs. If, on the other hand, the osmotic pressure of the solution is less than that of the cell sap, the protoplasm does not separate from the cell wall. Two solutions are therefore prepared, one of which just causes plasmolysis whereas the other just does not. The mean of these concentrations gives a solution of osmotic pressure equal to that of the cell sap—n other words, the solution is *isotonic* with the cell sap. Solutions of other salts may be prepared in a similar manner, and these are then not merely sotonic with the cell sap but also isotonic with one another.[3] By noting he dilutions required, the relative osmotic pressures of the original solutions can readily be calculated.

In a somewhat analogous manner isotonic solutions may be prepared by he aid of blood corpuscles, but for an account of the methods of procedure he reader is referred to the subjoined references.[4]

Osmotic Pressure and Raoult's Laws.—Indirect measurements of the osmotic pressures of dilute solutions may also be made by determination of the lowering of vapour pressure, elevation of boiling-point, or depression o freezing-point, since each of these magnitudes may be thermodynamically correlated with the osmotic pressure.[1] It is possible in this manner to obtain results of a high degree of accuracy when the requisite physical constants involved in the calculations are accurately known. For instance, the osmotic pressure in atmospheres of an aqueous solution at its freezing-point may be calculated from the equation

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[1] Berkeley, Hartley, and Stephenson, *loc. cit.*

[2] For the results of osmotic pressure measurements with various salts, see de Vries, *Zeitsch. physikal. Chem.*, 1888, **2**, 415 ; 1889, **3**, 103 ; Adie, *loc. cit* ; Berkeley, Hartley, and Stephenson, *loc. cit.*

[3] See Rysselberghe, *Réaction osmotique des cellules végétales*, Bruxelles, 1899 ; Prings-eim's *Jahrbücher wissenschaftliche Botanik*, 1884, **14**, 27 ; also de Vries, *loc. cit.*

[4] Hamburger, Dubois-Reymond's *Archiv*, physiologische Abt., 1886, p. 476 ; 1887, 31 ; *Zeitsch. physikal. Chem.*, 1890, **6**, 319 ; *Zeitsch. Biologie*, 1889, **26**, 414. Lob, *Zeitsch. physikal. Chem.*, 1894, **14**, 424. Grijns, *Verslagen Kon. Akad. Wetensch. Amst.*, eb. 1894 ; Pflüger's *Archiv*, 1896, **63**, 86. Hedin, *Zeitsch. physikal. Chem.*, 1895, **17**, 34 ; Pflüger's *Archiv*, 1895, **60**, 360. Koppe, *Zeitsch. physikal. Chem.*, 1895, **16**, 261. assart, *Archives de Biologie*, Belges, 1889, **9**, 15. Wladimiroff, *Archiv Hygiene*, 1891,), 81 ; *Zeitsch. physikal. Chem.*, 1891, **7**, 521. A very good account of several of these ethods is given by E. Cohen, *Physical Chemistry*, translated by M. H. Fischer (Bell & Sons, 1903) ; J. C. Philip, *Physical Chemistry* (Arnold, 2nd edition, 1913).

$$P = 12{\cdot}06\Delta - 0{\cdot}021\Delta^2,$$

where Δ denotes the depression of the freezing-point.[2]

It may be shown[3] that for dilute solutions the osmotic pressure, P, is connected with the lowering of vapour tension by the equation—

$$P = \frac{p - p'}{p} \cdot \frac{RTs}{M},$$

or more exactly by the equation—

$$P = \log_e \frac{p}{p'} \cdot \frac{RTs}{M},$$

where p and p' are the vapour tensions of solvent and solution respectively at the absolute temperature T, s is the specific gravity of the solvent, R is the gas constant, and M is the molecular weight of the solvent in the gaseous state.

The osmotic pressure of a dilute solution is connected with the lowering of freezing-point, Δ, by the formula

$$P = \frac{1000sL\Delta}{24{\cdot}17T},$$

where L is the latent heat of fusion of the solvent in calories and T the (absolute) freezing-point of the solvent.

The same formula is applicable if Δ denotes the elevation of boiling-point, L the latent heat of vaporisation, and T the (absolute) boiling-point of the solvent (the solute being supposed non-volatile).[4]

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[1] See, for instance, Van't Hoff, *loc. cit.*; Whetham, *Solutions* (Cambridge University Press, 1902); Nernst, *Theoretical Chemistry*, translated by Tizard (Macmillan & Co., 3rd edition, 1911); Lewis, *J. Amer. Chem. Soc.*, 1908, **30**, 668; and the references cited on p. 209.

[2] Lewis, *loc. cit.*

[3] Van't Hoff, *loc. cit.*; Arrhenius, *Zeitsch. physikal. Chem.*, 1889, **3**, 115; Nernst, *opus cit.*; Whetham, *opus cit.*

[4] For a further account of osmotic pressure, see Findlay, *Osmotic Pressure* (Longmans & Co., 1913). An account of the experimental methods used by Pfeffer, Morse, and Berkeley and Hartley is given by Lowry in *Science Progress*, 1913, **7**, 544.

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CHAPTER IV.

MOLECULAR WEIGHT AND ITS DETERMINATION.

THE terms "molecule" and "molecular weight" have already been defined in the first chapter of this volume. Although much evidence of the reality of molecules now exists,[1] no methods of measurement have yet been devised for the accurate determination of their absolute masses. In chemistry, however, one is concerned almost exclusively with the comparison of molecular weights. Accepting Avogadro's Hypothesis as a fundamental principle, this comparison can be readily accomplished by methods which were indicated by Avogadro and finally established through the clear exposition of the hypothesis by Cannizzaro.

Nearly thirty years after Cannizzaro's system was published, Van't Hoff proved that substances in solution exhibit an analogy to gases, being amenable to the gas laws, and therefore to Avogadro's Hypothesis. A method was thus discovered by which their molecular weights might be compared.[2]

No such generalisation, however, has yet been discovered for liquids. Various methods of comparing the molecular weights of substances in the liquid state have been devised, and some of them are discussed in this chapter, but none gives more than approximate values. Of the molecular state of solids still less is known, and no attempt has been made to describe any of the methods which have been suggested for its investigation. Moreover, the modern theory of crystal structure indicates that in the case of crystalline solids the term "molecule" has little significance.[3]

The determination of molecular weights is a necessary preliminary to a knowledge of the atomic weights of the elements,[4] but only in the cases of substances gaseous at ordinary temperature can exact molecular weights be directly determined. In the majority of cases it is necessary to determine approximate molecular weights of elements and compounds, and also the accurate chemical equivalents of the elements. From these two sets of data the accurate atomic weights of the elements and the molecular formulæ of the elements and compounds can be deduced. Exact molecular weights are then derived by adding together for each substance the relative weights of the atoms present in the molecule.

As obtained by physical measurements, molecular weights do not always correspond with the simplest formulæ that can be assigned to the substances concerned. Thus, knowing the atomic weights of mercury and chlorine, respectively, an analysis of mercurous chloride would lead us to assign the formula HgCl to the substance. The molecular weight determined by the vapour density,[1] however, indicates the formula to be Hg_2Cl_2. Likewise, cuprous chloride is Cu_2Cl_2, not CuCl; and nitrogen peroxide at ordinary temperature N_2O_4, rather than NO_2. In the majority of cases, especially when the molecular weights are derived from vapour densities, the molecular weights and molecular formulæ correspond to the simplest chemical values. On this account, values which are not identical with the simplest possible are often spoken of as *abnormal*. According to this usage, mercurous, cuprous, and aluminium chlorides and nitrogen peroxide provide examples of substances exhibiting abnormal molecular weights. But the vapour densities of aluminium chloride and nitrogen peroxide decrease with rise of temperature, until at length the values obtained correspond with the simplest formulæ $AlCl_3$ and NO_2. Such substances may, therefore, be regarded as made up of molecules which, in certain circumstances, possess the power of aggregating or associating.

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[1] See, for example, the section on Colloid Chemistry (p. 78).

[2] See Chaps. III. and VI.

[3] Groth, *Introduction to Chemical Crystallography*, translated by Marshall (Gurney & Jackson, 1906), chap. 1.

[4] See Chap. VII.

THE MOLECULAR WEIGHTS OF GASES AND VAPOURS.

The molecular weights of gases are, according to Avogadro's Hypothesis, proportional to their relative densities. Some standard of comparison is therefore necessary, and, for the present, the element oxygen has been selected and assigned the molecular weight 32. If therefore D_0 represents the gas or vapour density compared with that of oxygen,[2] and M is the molecular weight of the substance,

$$M : 32 = D_0 : 1,$$

or

$$M = 32D_0.$$

If, again, the vapour density measurement is made relative to hydrogen, then, since the molecular weight of the latter is found to be 2·016 when that of oxygen is taken as 32,

$$M = 2{\cdot}016D_H,$$

where D_H is the density compared with hydrogen.

Or, again, in many cases, the gas is simply compared with air. In such a case,

$$M = 28{\cdot}95D_A,$$

D_A being the density compared with air, and 28·95 and 32 the numbers which express the relative densities of air and oxygen.

The process may be regarded in another and very simple way. For, since 32 grams of oxygen occupy, at 0° and 760 mm., a volume of 22,400 c.c., the molecular weight of a substance will be the weight (in grams) which in the gaseous form occupies 22,400 c.c. at normal temperature and pressure.

The methods available for the experimental determination of the densities of gases and vapours fall into two classes, according as they are capable of yielding exact or merely approximate results. Exact determinations are possible only when the substances are gaseous at ordinary temperatures.[3] Liquid and solid substances have to be vaporised, and the gas laws do not accurately describe the behaviour of vapours.

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[1] For the *dry* substance; see p. 142; also Vol. III.

[2] Of course, at the same temperature and pressure.

[3] See Ramsay and Steele, *Phil. Mag.*, 1903, [vi.], 6, 492.

The Exact Determination of Densities and of Molecular Weights of Gases.—It is possible to carry out such determinations with hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, nitrous oxide etc.

Regnault's method,[1] which was an improvement on that of Arago and Biot, and has itself been improved by subsequent workers, is employed and is as follows:—[2]

A glass globe of known capacity is carefully cleaned, dried, evacuated, and weighed. It is then filled with pure gas, at an observed pressure p and temperature T, and reweighed. The value of p is usually about 760 mm., and the value of T is almost invariably 0° C. During the weighings the globe is counterbalanced by a "dummy" globe made of the same kind of glass and being as nearly as possible of the same weight and external volume as the experimental globe. The surfaces of the two globes are always treated in precisely the same manner. In this way errors due to the hygroscopic nature of glass and to *changes* in the temperature and pressure of the air in the balance room are avoided.

In order to explain the method of calculation, suppose that the excess weight of the evacuated globe over its tare is w_1 grams, and that of the globe plus gas is w_2 grams. The approximate weight of gas is then $(w_2 - w_1)$ or w grams, say. It may be supposed that T is equal to 0° C. and that p is approximately 760 mm.

Now, the glass globe, being elastic, responds to pressure, so that the volume of the evacuated globe is a trifle smaller than that of the globe when filled with gas.[3] Let this diminution in volume of the globe, due to evacuation, be called e c.c. A correction to the weight w is clearly necessary. Assuming that 1 c.c. of air under laboratory conditions weighs a grams, the upward force of the atmosphere on the globe, when filled at atmospheric pressure, exceeds that on the exhausted globe by ae grams. The corrected weight of the gas is therefore $w + ae$ grams.[4]

The volume of the globe is deduced from the weight of water that it holds. If the apparent weight of water (corrected if necessary for the weight of air displaced by the water) filling the globe at 0° C. is W grams, and d is the density of water at 0° C., the volume of the globe at 0° C. is W/d c.c. = V litres, say.

Hence, assuming the validity of Boyle's Law, the weight L of 1 litre of gas at 0° C. and 760 mm. is given by—

$$L = \frac{760(w + ae)}{pV} \text{ grams.}$$

In order to deduce the weight of a "normal litre," *i.e.* the weight of 1 litre of the gas at 0° C. and 760 mm. pressure, at sea-level in lat. 45°, the above value of L must be divided by—

$$(1 - 0{\cdot}0026 \cos 2\lambda - 0{\cdot}000000196h),$$

---

[1] Regnault, *Compt. rend.*, 1845, **20**, 975.

[2] For a more detailed account, see Chap. VII.

[3] Rayleigh, *Proc. Roy. Soc.*, 1888, **43**, 356; the correction thus shown to be necessary to the results of all previous work was applied to Regnault's results by Crafts (*Compt. rend.*, 1888, **106**, 1662).

[4] The measurement of e is described in Chap. VII. (p. 260).

where λ = latitude of laboratory and h = its height, in metres, above sea-level.

The value thus obtained is still subject to correction for at least two further sources of error: (i.) that owing to "adsorption" of gas by the inner surface of the globe, and (ii.) that introduced by assuming the validity of Boyle's Law. The first source of error causes the result to be high; its magnitude is small, and special methods are required to measure it.[1] For gases difficult to liquefy the correction may be ignored, but for easily condensible gases, such as hydrogen chloride, it should be determined if a high degree of accuracy is required. A number of experimenters have endeavoured to determine the influence of this source of error by measuring the density of the same gas in a number of different-sized bulbs. It would be expected that the measured densities would increase with a diminution in the size of the bulb. The results indicate that the magnitude of the error must be small, but yield no definite results concerning the extent of adsorption.[2] It is not possible to eliminate the error by weighing the globe filled with gas under a few mm. pressure instead of weighing it evacuated, since the extent to which adsorption occurs varies with the pressure (p. 108).

The second source of error may be rendered negligible by ensuring that the globe is filled with gas at a pressure which differs from 760 mm. only by a few mm. Otherwise, a correction is necessary, which can readily be applied if the compressibility of the gas at 0° C. is known.[3]

DENSITIES, CRITICAL TEMPERATURES, AND PRESSURES OF GASES.

Gas.	L.	L/L_{O_2}.	T_c.	P_c.
			° abs.	atmos.
Hydrogen	0·08987	0·06289	32	19·4
Nitrogen	1 2506	0·8752	128 0	33·6
Carbon monoxide	1·2503	0·8750	133·5	35·5
Oxygen	1·4290	1·0000	154·2	50·8
Nitric oxide	1·3402	0·9379	179 5	71·2
Methane	0 7168	0·5016	190·2	45·6
Carbon dioxide	1·9768	1·3833	304 0	72 9
Sulphur dioxide	2·9266	2·0480	430·2	77 7
Nitrous oxide	1·9779	1·3841	309·5	71·7
Hydrogen chloride	1·6392	1·1471	324 4	81·6
Ammonia	0·7708	0·5394	405·9	112·3
Phosphine	1·5293	1·0702	324·3	64·5
Ethane	1·3562	0·9191	305·1	48·9
Hydrogen sulphide	1·5392	1·0771	373·4	89 1
Methyl chloride	2·3045	1·6127	416 3	65·9
Methyl oxide	2·1096	1·4763	400·1	53·0

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[1] Burt and Gray, *Trans. Faraday Soc*, 1911, 7, 60.

[2] Baume, *J. Chim. phys.*, 1908, 6, 1; Guye and Davila, *Mém. Sci. phys. nat.*, 1908, 35, 635.

[3] It will be noticed that no allowance has been made for the weights of air displaced by the *weights* employed. This is not necessary if the relative values assigned to the various pieces are correct *in air*; if, however, in the calibration of the weights, all results had been reduced to the vacuum standard before the relative values of the pieces were calculated, the correction for air displaced by the weights becomes necessary.

In order to calculate exact molecular weights from the normal densities of gases, it is assumed that *at the same temperature, and under a common, indefinitely small pressure, all gases have exactly the same gram-molecular volume.* The calculation is then carried out as follows:—[1]

Let the common molecular volume of two gases be v_0, at 0° C., and under the infinitesimal pressure p_0. Their volumes will be different, v and v', say, at a pressure of one atmosphere, p_1. Now the deviations of the gases from Boyle's Law may be conveniently expressed as follows—

$$1 - \frac{p_1v_1}{p_0v_0} = A^{p_1}_{p_0}(p_1 - p_0) = A^1_0 \quad . \quad . \quad . \quad . \quad (1)$$

and

$$1 - \frac{p_1v'_1}{p_0v_0} = A'^{p_1}_{p_0}(p_1 - p_0) = A'^1_0,$$

in which A^1_0 and A'^1_0 represent the mean deviations of the gases from Boyle's Law between 0 and 1 atmosphere. Hence—

$$p_1v_1 = (1 - A^1_0)p_0v_0, \quad p_1v'_1 = (1 - A'^1_0)p_0v_0,$$

and therefore

$$\frac{v_1}{v'_1} = \frac{1 - A^1_0}{1 - A'^1_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If, then, the "normal" densities (*i.e.* weights of a "normal" litre) of the gases are L and L′ respectively, their molecular weights M and M′ satisfy the equation—

$$\frac{M}{M'} = \frac{(1 - A^1_0)L}{(1 - A'^1_0)L'},$$

which, if M′, L′, A'^1_0 refer to oxygen, may be written—

$$M = 32 \cdot \frac{L}{L_{O_2}} \cdot \frac{(1 - A\ )}{(1 - A_{O_2})} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

the limits zero and one atmosphere between which A is determined being understood. This equation expresses the molecular weight of a gas in terms of its density and compressibility, and the corresponding values for oxygen.

The determination of A^1_0 involves an extrapolation, but this is easily carried out in the case of gases that are difficult to liquefy, since, over the range of pressure from 1 to 2 or 3 atmospheres, the relationship between pv and p is linear. Moreover, the numerical values of A^1_0 for these gases are very small, and a very high order of accuracy in their measurement is not necessary. With gases such as carbon dioxide, hydrogen chloride, etc., that are readily liquefied, the values of A^1_0 are much greater and require to be determined with a considerable degree of precision. At the present time it cannot be said that such measurements have been accomplished. The relation between pv and p is not linear, the graph showing a slight, but decided curvature; and the only really satisfactory method of deducing A^1_0 consists in accurately measuring the values of pv from $p = 1$ atmosphere downwards as far as it is possible to obtain exact measurements. Graphic extrapolation then furnishes the limiting value p_0v_0. The only data at present (1914) available refer to hydrogen chloride [1] and selenide and to neon and helium.[2] Of the other methods that have been proposed, reference may be made to that employed by Baume,[3] in which the value of A_0^1 is deduced from density measurements made at various pressures, and to the various methods put forward by D. Berthelot,[4] of which that based on the approximate relationships—

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[1] D. Berthelot, *Compt. rend.*, 1898, 126, 954.

$$A_0^1 = \frac{A_{0.5}^1}{1 + A_{0.5}^1} \text{ and } A_0^1 = \frac{A_2^1}{1 + 4A_2^1},$$

is the simplest.[5]

The following table shows the results obtained by this method for a number of gases. The molecular weights, M″, calculated from the International Atomic Weights are included for comparison.

Gas.	$10^5 . A_0^1$.	M.	M″.	Gas.	$10^5 . A_0^1$.	M.	M″.
H_2 .	− 56	2·0155	2·016	HCl .	+ 743	36·469	36·468
N_2 .	+ 44	28·019	28·020	CO_2 .	+ 676	44·009	44·000
CO .	+ 60	28·009	28·000	N_2O .	+ 739	44·007	44·020
NO .	+ 114	30·006	30·010	C_2H_6 .	+ 1194	30·037	30·048
CH_4 .	+ 175	16·039	16·032	$(CH_3)_2O$	+ 2587	46·064	46·048

For densities, see p. 131; the value of A_0^1 for oxygen $= 96 \times 10^{-5}$.

The agreement is, in general, very good, and it is easy to deduce from the preceding results the atomic weights H = 1·00775, N = 14·007 (mean of 14·010, 14·006, 14·004), C = 12·005 (mean of 12·009, 12·006, 12·009, 11·995) and Cl = 35·460, in good agreement with the values obtained by gravimetric analysis.

The preceding method is known as the *Method of Limiting Densities*. Another method of calculating exact molecular weights has been given by Guye.[6] Van der Waals' equation (p. 31)—

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \quad . \quad (4)$$

becomes, when p is expressed in atmospheres, and the unit of volume is taken as the volume occupied by the gas at N.T.P.,

$$\left(p + \frac{a}{v^2}\right)(v - b) = \frac{(1 + a)(1 - b)}{273} . T \quad . \quad . \quad . \quad . \quad (5)$$

Guye and Friderich,[7] and also Van der Waals, have deduced from this equation that the relative molecular volumes of different gases at N.T.P. are proportional to

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[1] Gray and Burt, *Trans. Chem. Soc.*, 1909, 95, 1633.

[2] Bruylants and Bytebier, *Bull. Acad. roy. Belg.*, 1912, p. 856 (H_2Se); Burt, *Trans. Faraday Soc.*, 1910, 6, 19 (He and Ne).

[3] Baume, *J. Chim. phys.*, 1908, 6, 57–62.

[4] D. Berthelot, *Compt. rend.*, 1898, 126, 1030; 1907, 144, 76, 269; 145, 180, 317.

[5] The various methods proposed for determining A_0^1 are reviewed by Baume, *J. Chim. phys.*, 1908, 6, 52; Guye, *ibid.*, 1908, 6, 778–87; and Little, *Science Progress*, 1913, 7, 504.

[6] Guye, *J. Chim. phys.*, 1905, 3, 321.

[7] Guye and Friderich, *Arch. Sci. phys. nat.*, 1900, (iv.), 9, 505.

$$\frac{1}{(1+a)(1-b)},\quad \frac{1}{(1+a')(1-b')},\quad \frac{1}{(1+a'')(1-b'')},\ \text{etc.}$$

Hence,

$$M = \frac{KL}{(1+a)(1-b)},$$

where K is a constant for all gases. It is obviously the volume in litres occupied by a gram-molecule of perfect gas at N.T.P. For K, Guye adopts the value 22·412. Hence,

$$M = \frac{22{\cdot}412L}{(1+a)(1-b)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The values of a and b may be calculated[1] from the equations,[2]

$$T_c = 8a/27bR,\ p_c = a/27b^2,$$

in which, as has been already found above,

$$R = (1+a)(1-b)/273.$$

Now Van der Waals' equation is only approximately correct, and in order to obtain a more accurate representation of the behaviour of gases, it is necessary to assume that a and b vary with the temperature. For this purpose Guye employs the following empirical formulæ to deduce the values of a_0 and b_0, the values of a and b at 0° C.:—

$$a_0 = a\left(\frac{T_c}{T}\right)^{3/2},\quad b_0 = b\left(1 + \frac{T_c - T}{T_c}\right)\left(1 - \beta\cdot\frac{p_c}{p}\right) \quad . \quad . \quad . \quad (7)$$

The value of β, deduced from the critical constants, density and molecular weight of carbon dioxide, is 0·0032229 The molecular weight M is then given by the formula

$$M = \frac{22{\cdot}412L}{(1+a_0)(1-b_0)}.$$

A simpler method of calculation suffices for the difficultly liquefiable gases. The relations (7) above are not necessary, the equation

$$\frac{M}{L}(1+a)(1-b) = 22{\cdot}412 + mT, \quad . \quad . \quad . \quad . \quad (8)$$

being sufficiently accurate. The value of m, obtained by substituting the known data for oxygen, is 0·0000623.

The preceding method is known as the *Method of Reduction of Critical Constants*. It is an empirical method, and being based upon Van der Waals' equation, it would be expected to break down for gases that are at all associated at the critical temperature. The following table illustrates the nature of the results it yields:—

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[1] The calculation, which involves the solution of a cubic equation, is conveniently effected by the method given by Haentschel, *Ann. Physik*, 1905, [iv.], **16**, 565.

[2] Deduced from Van der Waals' equation.

Gas.	$10^5 . a$	$10^5 . b$.	$10^5 . a_0$.	$10^5 . b_0$.	M.	M″.
H_2	29	74	...		2·015	2·016
N_2	275	174	...	...	28·013	28·020
CO	284	172			28·003	28·000
NO	257	115	..	...	30·009	30·010
CH_4	379	160	...	...	16·034	16·032
CO_2	721	191	847	161	44·002	44·000
N_2O	719	185	878	156	44·012	44·020
NH_3	859	170	1554	146	17·036	17·034
HCl	722	179	937	152	36·451	36·468
H_2S	900	194	1438	240	34·085	34·076
C_2H_6	1209	314	1449	299	30·051	30·048

For values of L, T^c, and P_c, see p. 131; M and M″ as before.

Reference only can be made to Leduc's *Method of Molecular Volumes* and Guye's *Method of Corresponding Densities.*[1]

Approximate Determination of Gas Densities: Bunsen's Diffusion Method.—This method[2] was introduced by Bunsen to determine approximately the density of a gas when only a few cubic centimetres were available. It is based on Graham's Law of Diffusion.

If d_1 and d_2 are the densities of two gases, v_1 and v_2 their rates of flow under the same difference of pressure through a small aperture, then $\frac{v_1^2}{v_2^2} = \frac{d_2}{d_1}$.

The velocity of flow will be inversely proportional to the time taken for equal volumes to diffuse. Hence, if t_1 and t_2 are the times required, in seconds, for equal volumes of the gases to flow through the aperture, $\frac{t_1^2}{t_2^2} = \frac{d_1}{d_2}$. If d_1 is known, d_2 can be found.

The apparatus employed consisted of a glass tube open at the lower end, and closed by a tap at the upper end. Just beyond the tap, the tube, contracted to a small diameter, was closed by a sheet of platinum containing a hole so small as to be invisible to the naked eye. The tube was filled with and inverted over mercury, and the gas introduced, the level of the mercury outside being sufficiently above that within the tube to drive the gas steadily forward. The tap was now opened and the time required for the mercury level to rise through a certain height in the tube (determined by the aid of a float) was noted. By a comparison under exactly the same conditions with a gas of known density, the density of the first gas could then be found.

More recently, Emich[3] has modified the method for use at high temperatures (1400°–2000°). It has also been used at the ordinary temperature by Debierne[4] in the determination of the density of niton (radium emanation).

The Approximate Determination of Vapour Density.—For the determination of the vapour densities of substances which exist normally as liquids or solids, three methods are still in use, viz. those devised by Dumas, by Hofmann, and by Victor Meyer respectively.

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[1] Leduc, *Ann. Chim. Phys.*, 1898, [vii.], **15**, 5; 1910, [viii.], **19**, 441; Guye, *Compt. rend.*, 1905, **140**, 1386. The various methods for determining exact molecular weights have been reviewed by Guye (*J. Chim. phys.*, 1908, **6**, 769); Little, *Science Progress*, 1913, **7**, 504.

[2] Bunsen, *Gasometrische Methoden*, 1857, p. 128.

[3] Emich, *Monatsh.*, 1903, **24**, 747; 1905, **26**, 505 and 1011.

[4] Debierne, *Compt. rend.*, 1910, **150**, 1740.

In the first-named method[1] the substance to be volatilised is introduced into a weighed round, pear-shaped or cylindrical bulb, the neck of which is drawn out to a point. The bulb is heated by means of a constant temperature bath maintained at about 20°–30° above the boiling-point of the substance under investigation until the air has been swept out of the bulb and all excess of the material also removed. The end of the neck is then quickly sealed, the temperature and barometric pressure noted, the bulb allowed to cool and then weighed. After the weight has been recorded, the bulb is immersed in air-free distilled water at the laboratory temperature, or in mercury, and the point of the neck nipped off. The weight of liquid filling the bulb is then obtained, the weight of the air contained in the bulb when originally weighed being neglected, as it is small in comparison with the weight of the liquid.

The vapour density of the substance may now be calculated. If w_1 is the weight of the bulb filled with air, w_2 the weight when filled with the vapour, and w_3 the weight when filled with water, then $w_3 - w_1$ = weight of water filling the bulb (neglecting weight of air, as already mentioned).

If the weight is expressed in grams, the number, so far as an approximate determination is concerned, expresses also the capacity of the bulb in c.c. If, then, d be the density of the air in grams per c.c., the weight of air which the bulb contained is $(w_3 - w_1)d$, and the weight of the bulb itself $w_1 - (w_3 - w_1)d$. Hence the weight of the vapour is $w_2 - [w_1 - (w_3 - w_1)d]$.

The weight of the vapour and its volume now are known and the density can be deduced.[2]

A more accurate development of Dumas' method permits of the determination of vapour densities at various pressures according to the amount of substance initially taken. The apparatus consists of a glass (or quartz) vaporisation bulb of known capacity, fused into which is a flattened spiral tube. Increase of the internal pressure causes the spiral to distend, whilst contraction is induced by raising the external pressure. The internal pressure can clearly be determined by adjusting the external pressure, the deflections being observed by means of a small mirror. After the introduction of the material, the bulb is evacuated and sealed. Upon raising the temperature the pressure observed is that due to the vaporised material.[3]

In the Hofmann method[4] a known weight of the substance is volatilised in the space above the mercury in a calibrated barometer column, jacketed with a vapour tube at some constant temperature. The amount of the substance required is small and is passed to the surface of the mercury column in a small glass-stoppered tube, in such quantity as to leave no portion unvolatilised. Fig. 63 shows the form of apparatus used by Young.[5] By means of this apparatus a series of readings can be made at different temperatures by varying the pressure of the vapour contained in the jacket, and by connecting the closed mercury reservoir to a second pump the pressure on the vaporised substance in the barometer tube can likewise be altered at will.

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[1] Dumas, *Ann. Chim. Phys.*, 1826, [ii.], 33, 337.

[2] Most of the results recorded in the literature are expressed as densities relative to air. As examples of the use of the method, see Friedel and Crafts, *Compt. rend.*, 1888, 106, 1764; Nilson and Pettersson, *Zeitsch. physikal. Chem.*, 1889, 4, 206; *Ann. Chim. Phys.*, 1890, [vi.], 19, 145; Biltz, *Ber.*, 1901, 34, 2490; Biltz and Preuner, *Zeitsch. physikal. Chem.*, 1902, 39, 323.

[3] Johnson, *Zeitsch. physikal. Chem.*, 1908, 61, 457; Preuner and Schupp, *ibid.*, 1909, 68, 129; Preuner and Brockmöller, *ibid.*, 1912, 81, 129; Bodenstein and Katayama, *ibid.*, 1909, 69, 26; Jackson, *Trans. Chem. Soc.*, 1911, 99, 1066.

[4] Hofmann, *Ber.*, 1868, 1, 198.

[5] Young, *Proc. Phys. Soc.*, 1895, 13, 658. See Thorpe, *Trans. Chem. Soc.*, 1880, 37, 147.

In any case, the material is volatilised at a pressure less than atmospheric, and substances which undergo decomposition when heated at atmospheric pressure can be investigated by this method. If the barometric pressure is P mm., the height of the mercury column (corrected for temperature) h mm., then the pressure at which the vapour exists is $P - h$ mm. The volume is read on the calibrated barometer tube.

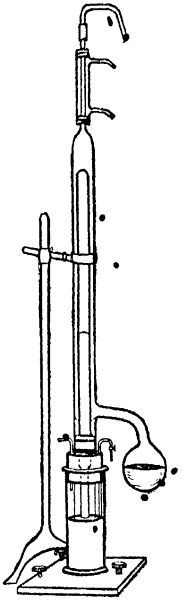

Fig. 63.—Young's modification of Hofmann's vapour density apparatus.

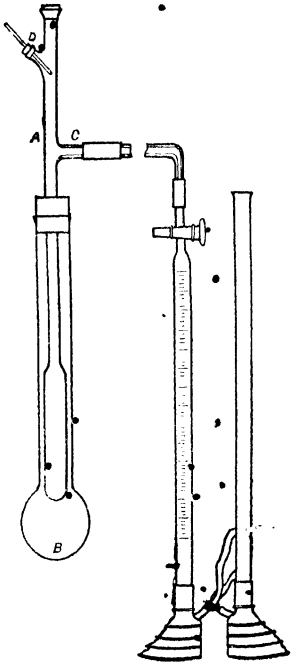

Fig. 64.—Victor Meyer's vapour density apparatus.

The process requires much smaller quantities of material than that of Dumas, but cannot be used at temperatures over 250° owing to the vapour tension of mercury becoming then considerable. Above 100° a correction for the mercury vapour present should be made.

Of the three methods, that of Victor Meyer[1] is the one available over the greatest range of temperature and the one used in most modern investigations. The apparatus (fig. 64) consists essentially of the vaporisation tube A, closed at the top by a stopper, and terminating in a cylindrical bulb at the lower end. Outside the heating jacket B, a side tube C is attached to A, connecting it with a gas burette or eudiometer tube. A glass rod, fitted through a side tube in the head of the apparatus, serves as a support for the small capsule, glass bulb, or stoppered bottle containing a weight of the substance sufficient to give 20 to 30 c.c. of vapour. Constant temperature is maintained in the cylindrical bulb by the vapour of a suitable liquid boiled in B; and when once obtained, as shown by a constant reading in the gas burette, the glass rod at D is drawn back and the vessel with the substance allowed to fall on to a pad of sand or asbestos in the bottom of the bulb. Rapid vaporisation occurs, and, owing to the length of the bulb and narrowness of the tube, air is expelled instead of vapour through C, and collected and measured at the temperature of the gas burette, the pressure being the barometric, corrected for the vapour tension of the water in the collecting tube. The temperature is ascertained by suspending a thermometer in contact with the gas-collecting apparatus or in the water jacket, with which it is best to surround the measuring apparatus to preserve constancy of temperature.

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[1] V. Meyer, *Ber.*, 1878, 11, 2253.

If w is the weight in grams of substance vaporised, v the volume in c.c. of gas observed, p the barometric pressure in mm., f the vapour tension of water at t° C. (the temperature of the experiment), the vapour density relative to hydrogen and oxygen is given by the following expressions:—[1]

(*a*) relative to hydrogen, $$\frac{w \times (273 + t) \times 760}{v \times (p - f) \times 273 \times 0{\cdot}0000899},$$

(*b*) relative to oxygen, $$\frac{w \times (273 + t) \times 760}{v \times (p - f) \times 273 \times 0{\cdot}001429}.$$

It is necessary that vaporisation of the substance shall occur at a rapid rate; otherwise the vapour will, by slow diffusion, find its way up the vaporisation tube, be carried forward with the air expelled, and condense when cooled, thus reducing the volume of air which ought to be obtained in the burette. To obtain rapid vaporisation, the bulb should be maintained at a temperature not less than 30° above the boiling-point of the substance. Thus, if steam is the heating medium in the jacket, a successful determination could be easily carried out with carbon disulphide (B. Pt. 46°), but probably not with ethyl alcohol (B. Pt. 78°).

Various modifications of the method have been devised. Instead of measuring the volume of gas expelled, Lumsden determines the increase of pressure associated with the vaporisation of the substance, the volume of the apparatus being maintained constant.[2]

Determination of Vapour Density at High Temperatures.—Both the Dumas and the V. Meyer methods may be used at high temperatures.

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[1] These formulæ hold when the air initially present in the apparatus was dry. If, however, the pressure of aqueous vapour in the initial air was x per cent. of the pressure of saturated aqueous vapour at t°, the factor $(p-f)$ should be replaced by $\left(p - \frac{100-x}{100} \cdot f\right)$. See Evans, *J. Amer. Chem. Soc.*, 1913, **35**, 958.

[2] For details of the method, see Lumsden, *Trans. Chem. Soc.*, 1903, **83**, 342.

In the former, porcelain may be substituted for glass, and for the latter, which is the more useful method, modifications are described below.

Up to 600°, constant temperatures can be maintained by a vapour bath, for which purpose, aniline (B. Pt. 184°), diphenylamine (B. Pt. 310°), sulphur (B. Pt. 445°), phosphorus pentasulphide (B. Pt. 518°), and stannous chloride (B. Pt. 606°) are all available. At still higher temperatures, Meyer used specially constructed gas furnaces (see references below), whilst in the subsequent investigations of Nernst and v. Wartenberg, in which temperatures of 2100° were attained, the electric furnace has been adopted for the same purpose.

For high temperatures the vaporisation tube may be constructed of porcelain,[1] of platinum,[2] of platinum and iridium alloyed, or of iridium alone.[3] Above 1700° porcelain begins to soften and must be protected by a platinum covering, whilst platinum and iridium are permeable to gases at high temperatures and must be rendered impermeable by a non-porous coating, obtained in v. Wartenberg's experiments by applying a fused mixture of magnesium oxide and chloride.

Air cannot be used to fill the apparatus in any case where the substance readily undergoes oxidation, and, as a rule, is not used at high temperatures. Nitrogen or hydrogen is generally employed, sometimes carbon dioxide, whilst v. Wartenberg used argon.

Since in Meyer's method the gas expelled is measured at the ordinary temperature, the temperature of evaporation need not be ascertained. But as many substances change their molecular state, and hence their density, as the temperature changes, it is obviously of interest to record the temperature. At high temperatures, Mensching and Meyer[4] swept out the gas (*e.g.* nitrogen) remaining after the density determination by a stream of hydrogen chloride, and from its amount and the original capacity of the vaporisation tube determined in like manner, the temperature was calculated from the known coefficient of expansion of the gas, after allowing for the amount of the gas expelled by the vaporised substance and for various corrections, for the evaluation of which the reference may be consulted. Biltz and Meyer[5] used the simpler, though somewhat less accurate, process of collecting the gas expelled from the moment when heating began to that at which the substance was introduced, and from the amount expelled, calculated, as before, the temperature attained. The vaporisation tube served, therefore, not only its original purpose, but acted in addition as an air thermometer. In the experiments of Nernst and of v. Wartenberg the temperatures were measured photometrically by comparing the light emitted by the heated bulb with that from a standard source of light.

Consideration of Results. Molecular Formulæ.—After the molecular weight of a substance has been arrived at, the molecular formula may be determined by comparison of the molecular weight with the empirical formula weight. Thus, to quote once again the example of mercurous chloride, chemical analysis indicates that the amounts of chlorine and mercury present are related as represented by the empirical formula HgCl. The molecular formula, corresponding to the molecular weight, may be written as $(HgCl)_n$ where n is the ratio of the molecular weight to the empirical formula weight. In this particular case $n = 2$, or the molecular formula of mercurous chloride is Hg_2Cl_2. In a very large number of cases, however, n is found to be unity, which means that the molecular weights in such cases correspond with the simplest possible chemical formulæ.

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[1] Mensching and Meyer, *Ber.*, 1886, **19**, 3295.

[2] Dewar and Scott, *Proc. Roy. Soc.*, 1879, **29**, 490; Mensching and Meyer, *Zeitsch. physikal. Chem.*, 1887, **1**, 145.

[3] Nernst, *Zeitsch. Elektrochem.*, 1903, **9**, 622; H. v. Wartenberg, *Zeitsch. anorg. Chem.*, 1908, **56**, 320. In these investigations the bulb of the vaporisation tube was reduced to 2·5-3 c.c.

[4] Mensching and Meyer, *Zeitsch. physikal. Chem.*, 1887, **1**, 145.

[5] Biltz and Meyer, *ibid.*, 1889, **4**, 249.

Consider now the formulæ for the chemical elements. The simplest formulæ are, for example, H, O, Cl, N, A, P, S, Hg, etc.—symbols which represent atoms of these substances. Whether or not the symbols also represent molecules is decided when the molecular weights of the elements are known; and until they are known, the molecular formulæ can only be written H_n, O_n, etc. Avogadro showed, by the application of the principle which he introduced, that the oxygen molecule contains two atoms and is therefore O_2, and Cannizzaro, by the use of the same principle, came to the conclusion that most elementary molecules were polyatomic, generally diatomic, but that phosphorus and arsenic were tetratomic, and, on the other hand, mercury was monatomic.

At the present time the following elements are definitely recognised as monatomic from vapour density measurements: mercury,[1] cadmium,[2] zinc,[3] lead,[4] as well as the inert gases of the atmosphere, helium, argon, neon, krypton, xenon, and niton. The molecular formulæ of these substances are, accordingly, Hg, Na, K, Cd, Zn, Pb, He, A, Ne, Kr, Xe, and Nt. Almost all the metals which have been vaporised possess monatomic molecules.

Oxygen, hydrogen, nitrogen, chlorine,[5] bromine,[6] and, below 600°, iodine, have molecular weights such that the formulæ O_2, H_2, N_2, Cl_2, Br_2, I_2 represent them. For phosphorus, arsenic, and antimony, the formulæ P_4, As_4, and Sb_4 correspond to the molecular condition of these elements unless the temperature is very high.

For compounds the molecular and empirical formulæ coincide as a rule. The following are well-known examples. H_2O (see below), H_2S, HCl, N_2O, NO, CO_2, etc.; and among salts, KI,[7] KCl,[8] and $PbCl_2$.[9] On the other hand, cuprous chloride, from vapour density measurements, must be represented by the formula Cu_2Cl_2,[10] and mercurous chloride by Hg_2Cl_2.

Two factors, however, have a considerable bearing on the size of the molecule—namely, the temperature and the pressure. Rise of temperature or decrease of pressure tends to break up the large molecules into smaller ones, and the *dissociation*, as the process is termed, may follow one of two courses in producing like parts on the one hand, and unlike parts on the other.

Molecular Association and Dissociation: (*a*) *The Influence of Temperature.*—From the above it is evident that the choice of a molecular formula is not in many cases as simple as may be supposed, for the molecular weight, and therefore the formula, of a substance depends to a considerable extent on the temperature at which it is examined. Many substances exhibit the power of becoming associated, or of forming molecular aggregates. Even water vapour, the formula of which is always written as H_2O, is not entirely in the simple condition which this formula indicates. Rather, there is a balance between the associated and the dissociated molecules which may be represented by the equation $(H_2O)_2 \rightleftharpoons 2H_2O$, assuming the association to proceed no further than to double molecules, the equilibrium depending on the temperature and the pressure. Bose[1] calculates that the simple molecules are present to the extent of 93·4 per cent. at 0°, 91·1 per cent. at 100°, and 91·3 per cent. at 200°, the pressures being the vapour pressures corresponding to these temperatures A better known case is the equilibrium expressed by $N_2O_4 \rightleftharpoons 2NO_2$. At 150°, and at atmospheric pressure, the gas is made up entirely of simple molecules, NO_2, but as the temperature is reduced below this value, association occurs until at the boiling-point (22°), the vapour consists almost wholly of N_2O_4 molecules. At intermediate temperatures, a mixture of the two forms exists. Still more striking is the case of sulphur vapour. H. v. Wartenberg found the molecular weight at 2070° to be 50, corresponding therefore to a mixture of S_2 and S molecules; at 1719° the molecule is S_2,[2] whilst at the boiling-point (445°) the vapour consists of molecules which are most nearly represented by the formula S_8.[3] In like manner, the molecules P_4, As_4, and Sb_4, tend to pass, with elevation of temperature, into smaller molecules, P_2, As_2, and Sb_2,[4] and, according to v. Wartenberg's measurements[5] with antimony, into still simpler molecules. The diatomic molecules Cl_2, Br_2, I_2 also begin to pass into monatomic molecules with rise of temperature, iodine even at as low a temperature as 600°.

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[1] Cannizzaro from Dumas' data.

[2] Dewar and Dittmar, *loc. cit.*

[3] Mensching and Meyer, *Ber*, 1887, 20, 1833.

[4] H. v. Wartenberg, *loc. cit.*

[5] For chlorine between 300° and 1450°; Pier, *Zeitsch. physikal. Chem.*, 1908, 62, 385.

[6] Below 800°; Ramsay and Young, *Trans. Chem. Soc.*, 1886, 49, 453.

[7] Mensching and Meyer, *Ber.*, 1887, 20, 582; Dewar and Scott, *loc. cit.*

[8] Nernst, *loc. cit.*

[9] Roscoe, *Ber.*, 1878, 11, 1196.

[10] V. Meyer and C. Meyer, *Ber.*, 1879, 12, 1283; H. Biltz and V. Meyer, *Zeitsch. physikal. Chem.*, 1889, 4, 266.

Among salts, aluminium chloride furnishes an excellent example, the following figures[6] denoting its vapour densities (compared with air) at various temperatures :—

Dumas' Method.		V. Meyer's Method.	
Temperature ° C.	V.D.	Temperature ° C.	V.D.
209°	9 90	440°	7 45
301°	9·55	518°	7·18
357°	9 34	606°	5·34
401°	9 02	758°	4·80
440°	8·79	1117°	4·27
		1400°	4·27

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[1] E. Bose, *Zeitsch. Elektrochem.*, 1908, **14**, 270.

[2] H. Biltz and V. Meyer, *Zeitsch. physikal. Chem.*, 1889, **4**, 266.

[3] In reality the vapour is a mixture of S_8 and S_6 molecules at temperatures in the neighbourhood of the boiling-point under normal pressure.

[4] Mensching and Meyer, *Annalen*, 1887, **240**, 317. H. Biltz, *Zeitsch. physikal. Chem.*, 1896, **19**, 385 ; H. Biltz and V. Meyer, *Ber.*, 1889, **22**, 725 ; Stock, Gibson, and Stamm, *Ber.*, 1912, **45**, 3527 ; Preuner and Brockmoller, *loc. cit.*

[5] Wartenberg, *loc. cit.*

[6] Nilson and Pettersson, *Zeitsch. physikal. Chem.*, 1889, **4**, 206.

For the formula Al_2Cl_6 the vapour density should be 9·24, for $AlCl_3$, 4·6.[1] The two methods do not give identical results, but the dissociation with rise of temperature is obvious. The reason for this discrepancy lies in the fact that in the Victor Meyer apparatus the aluminium chloride, when vaporised, is diffused in an inert gas and its mean partial pressure is thus considerably less than one atmosphere.

Other examples are provided by stannous chloride[2] and silver chloride.[3] All these are examples of the phenomenon of dissociation. A rise of temperature simplifies the molecular condition, giving rise to dissociation, and a lowering of temperature has the reverse effect.

Whereas the term "molecular association" is usually employed to indicate the union of two or more like molecules, the reverse process of dissociation includes also the separation into unlike molecules. In all the instances so far quoted—as for instance, nitrogen peroxide or aluminium chloride—molecules have separated or dissociated into like parts. But quite early in the determination of molecular weights by vapour density measurements examples of abnormal vapour densities of the second kind were found. Thus, mercurous chloride, according to the determinations of Mitscherlich[4] and of Deville and Troost,[5] had the formula HgCl; but Odling[6] observed that the vapour was a mixture of mercury and mercuric chloride, the mercurous chloride having dissociated into these substances. This naturally suggested that a molecule of mercurous chloride should be represented by Hg_2Cl_2, and the dissociation by the equation—

$$Hg_2Cl_2 \rightleftharpoons HgCl_2 + Hg;$$

and in 1900, Baker showed that mercurous chloride, when pure and dry, vaporises without dissociating, and that the molecular formula for the substance in the gaseous state is really Hg_2Cl_2, as had been supposed.[7]

Phosphorus pentachloride (PCl_5), ammonium chloride (NH_4Cl), and hydrogen iodide (HI) furnish other examples of substances having abnormal vapour densities due to a dissociation into the dissimilar parts, $PCl_3.Cl_2$, $NH_3.HCl$, and $H_2.I_2$ (from 2HI) respectively. Reference will be made to these substances in the subsequent volumes of this work, but it may be pointed out here that in several cases investigated, the occurrence of dissociation depends on the presence of traces of moisture. Ammonium chloride, for instance, can, like mercurous chloride, be vaporised without dissociation if perfectly dry.[8]

(*b*) *The Effect of Pressure.*—As has been already mentioned, dissociation is facilitated by diminution of pressure. This may be illustrated by reference to nitrogen peroxide, the dissociation of which may be readily followed by density measurements. If the observed vapour density with reference to oxygen be d, and if a fraction α of the N_2O_4 molecules has dissociated, then for each molecule of N_2O_4 initially present in the undissociated gas there are obviously $(1 - a) + 2a$ or $(1 + a)$ molecules of the mixed molecules. The theoretical vapour density of N_2O_4 is 2·875, and hence by Avogadro's Hypothesis,

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[1] See also Deville and Troost, *Ann. Chim. Phys.*, 1860, [iii.], 58, 257; *Compt. rend.*, 1857, **45**, 821; Nilson and Pettersson, *Zeitsch. physikal. Chem.*, 1887, **1**, 459; Friedel and Crafts, *Compt. rend.*, 1888, **106**, 1764.

[2] V. and C. Meyer, *Ber.*, 1879, **12**, 1195.

[3] H. Biltz and V. Meyer, *loc. cit.*

[4] Mitscherlich, *Pogg. Annalen*, 1833, **29**, 139.

[5] Deville and Troost, *Compt. rend.*, 1857, **45**, 821.

[6] Odling, *Quart. Journ. Chem. Soc.*, 1864, **17**, 211.

[7] See Vol. III. of this series.

[8] Baker, *Trans. Chem. Soc.*, 1900, **77**, 646; 1894, **65**, 612. On the behaviour of mercurous chloride, see also Smith and Menzies, *Zeitsch. physikal. Chem.*, 1911, **76**, 713; *J. Amer. Chem. Soc.*, 1910, **32**, 1541.

$$2{\cdot}875/d = 1 + a.$$

At a temperature of 49·7°, the following figures[1] record the values of the degree of dissociation (a) of the N_2O_4 molecule, at various pressures :—

Pressure.	a.	Pressure.	a.
0 mm.	1·000	182·69 mm.	0·690
26·80 ,,	0·930	261·37 ,,	0·630
93·75 ,,	0·789	497·75 ,,	0·493

The sulphur molecule S_8 likewise undergoes dissociation with decrease of pressure.[2]

THE DETERMINATION OF MOLECULAR WEIGHT IN SOLUTION.

From the analogy already discussed in Chap. III.[3] between the gaseous and dissolved states, a close resemblance between the methods of determining molecular weights in these two states is to be expected; and although the resemblance may not at first be obvious, a little consideration makes it clear.

The molecular weight of a gas is obtained by finding what weight of it occupies, at 0° and 760 mm, a volume of 22,400 c.c. The measurements made are temperature, pressure, and density (or concentration).

With a solution the problem is exactly the same, it being necessary to determine what weight of the substance, dissolved in 22,400 c.c. of the solvent, exerts at 0° an osmotic pressure of 760 mm. Again the measurements are temperature, pressure (osmotic), and the concentration (or, as it may be termed, the density, or mass of substance per unit volume).

The molecular weight of a dissolved substance could, of course, be obtained without any knowledge of the osmotic pressure laws, for Raoult's empirical laws concerning the depression of vapour pressure and of freezing-point make this possible. Indeed, the principles and methods introduced by Raoult are extensively used in molecular weight determination in solution. These laws, however, have their theoretical basis in the laws of osmotic pressure, and a measurement of the depression of vapour pressure or of the freezing-point of a solvent is only an indirect measurement of the osmotic pressure of the substance in solution.

The methods to be described here include those depending on the direct measurement of osmotic pressure, the depression of vapour pressure, the elevation of the boiling-point and depression of the freezing-point of solutions. In so far as dilute solutions are concerned the theory of these methods has been discussed in Chap. III. One other method of arriving at molecular formulæ, viz., the empirical method of Ostwald based on conductivity measurements, is also added.

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[1] E. and L. Natanson, *Wied. Annalen*, 1885, **24**, 454; 1886, **27**, 606.

[2] Biltz, *Ber.*, 1901, **34**, 2490; H. Biltz and Preuner, *Zeitsch. physikal. Chem.*, 1902, **39**, 323; Preuner and Schupp, *ibid.*, 1909, **68**, 129; Bleier and Kohn, *Monatsh.*, 1900, **21**, 575.

[3] See also Chap. VI.

Molecular Weight Determination from Osmotic Pressure.—The data required, as already stated, are the temperature, the osmotic pressure, and the concentration. The osmotic pressure can be determined by using a porous cell with an artificially prepared membrane, or by the methods of de Vries and of Hamburger, as already described in Chap. III.

As the results obtained with aqueous solutions of inorganic substances are abnormal, a phenomenon to be discussed later, some measurements made by Morse and Frazer on cane sugar may be used as an illustration. A solution of 6·84 grams of this substance in 100 grams of water was found to exert at 15° an osmotic pressure of 4·91 atmospheres.

It is required, then, to find the weight of sucrose, which, in 22,400 grams of water, would exert at 0° an osmotic pressure of 1 atmosphere Since the gas equation is true for dilute solutions, this weight M is given by

$$M = \frac{6{\cdot}84 \times (273 + 15) \times 22{,}400}{273 \times 100 \times 4{\cdot}91} = 329{\cdot}2,$$

as compared with the theoretical value 342 calculated from the formula $C_{12}H_{22}O_{11}$ and atomic weights of the elements. The error is no greater than is found in many cases when molecular weights are derived from vapour density determinations.

Raoult's Cryoscopic Method: the Depression of Freezing-Point.—As ordinarily practised, the method used contains various devices and improvements introduced by Beckmann, but the essential process is that of Raoult, and consists in measuring the freezing-point of a solvent, before and after adding a known weight of the substance whose molecular weight is required.

For very dilute solutions, platinum resistance thermometers give the most accurate results. Ordinarily, the Beckmann thermometer of mercury in glass, reading to 0·001°, is employed (fig. 65). This thermometer usually has a scale reading of only 5°–6°, and to obviate the necessity of having a large number of instruments suitable for different temperatures, the thermometer is so constructed as to be available for use at different temperatures. For this purpose, the upper end of the capillary bore opens out into a large reservoir into which mercury can be driven. If, for example, the amount of mercury in the bulb is sufficient to cause the thread to appear on the scale at 50°, less mercury will be required if the temperature to be measured is 60°. The instrument is accordingly heated to about 64° until the excess of mercury has been driven into the reservoir, and it will be found on cooling that the thread is visible on the scale at 60°. A slight correction is needed for the varying amount of mercury in the bulb.[1]

The freezing-point apparatus (fig. 66) consists of a stout glass tube fitted with a side tube, and closed at the top by a cork, through which pass the thermometer and stirrer (preferably of platinum). The side tube, also closed by a cork, serves for the introduction of the substance under investigation. Surrounding the freezing-point tube is a wider tube which serves as an air jacket and so prevents too rapid a fall of temperature, and finally the cooling-bath which may contain a freezing mixture, water only or other material, according to the freezing-point of the solvent. A known weight of the solvent is introduced into the freezing-point tube and the freezing-point determined, whenever possible, by the method of supercooling. For this purpose the solvent is cooled directly in the cooling-bath until solid begins to separate. The tube is then quickly dried, placed in its jacketing-tube, the liquid stirred slowly, and the temperature read off when it has become constant. An approximate value for the freezing-point being thus obtained, the tube is withdrawn from its mantle and the frozen solvent allowed to melt. It is then replaced in its jacket and the liquid stirred slowly while the temperature falls. When the temperature has fallen to 0·2°–0·5° below the approximate freezing-point, the liquid is stirred more vigorously, when crystallisation commences, and the temperature rises.[1] The liquid being slowly stirred, the temperature is read off every few seconds, the thermometer being tapped before each reading. The highest temperature reached is recorded as the freezing-point of the solvent. The freezing-point should be determined in three independent experiments and the mean value adopted.

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[1] See Ostwald-Luther, *Physico-chemische Messungen* (Leipzig, 3rd edition, 1910). For a description of various types of differential thermometers, see Beckmann, *Zeitsch. physikal. Chem.*, 1905, 51, 329.

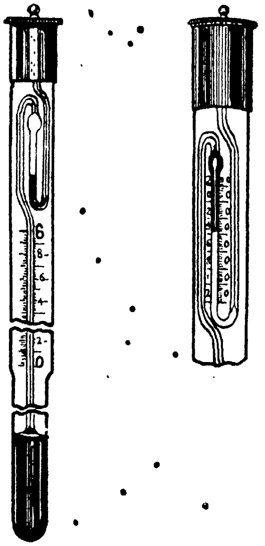

FIG. 65.—Beckmann thermometer.

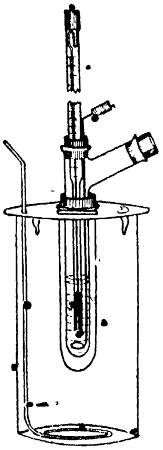

FIG. 66.—Beckmann freezing-point apparatus.

A weighed quantity of the solute (usually compressed by means of a small tabloid press) is then introduced through the side tube into the solvent and allowed to dissolve. The freezing-point of the solution is then determined as already described, an approximate value and then four or five accurate values being found.

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[1] If crystallisation does not commence, the liquid must be inoculated with a tiny crystal of the solvent.

A further addition of solute and another freezing-point determination are then made.

In order that reasonably accurate results may be obtained, the cooling-bath should not be more than 3° below the temperature at which the solvent freezes, the amount of supercooling of the solution should not exceed 0·2°–0·5°, stirring should be uniform and not too rapid, and the thermometer should always be smartly tapped before a temperature is read.

The calculation is made as follows: If w grams of a substance, dissolved in W grams of solvent, lower the freezing-point of the latter by $\Delta°$ C., the molecular weight M of the solute is given by

$$M = \frac{C.w}{\Delta.W},$$

where the value of the constant C depends only on the solvent.

The following are the values of the cryoscopic constant C for some commonly used solvents:—

Water	1860	Phenol	7300
Benzene	5000	Acetic Acid	3900
Nitrobenzene	7000	Formamide	3900

The constant C is equal to one hundred times the value of Raoult's "molecular depression of the freezing-point" (p. 122), which may be calculated, as was shown by Van't Hoff,[1] from the equation

$$\text{Molecular depression} = \frac{0{\cdot}02T^2}{L},$$

in which T denotes the freezing-point (absolute) of the solvent, and L its latent heat of fusion in calories per gram.

Molecular Weight by the Depression of Vapour Pressure.—Raoult's law of depression of vapour tension for dilute solutions of non-volatile solutes (see p. 114) may be written as

$$\frac{p_0 - p_1}{p_0} = \frac{n}{N}.$$

If w is the weight of the solute dissolved in W grams of solvent, m and M denote the molecular weights of solute and solvent respectively, $n = \frac{w}{m}$, and $N = \frac{W}{M}$, so that

$$\frac{p_0 - p_1}{p_0} = \frac{wM}{Wm},$$

and hence m can be found from measurements of the vapour tension.

The method is not used very extensively for inorganic solutes, and is mainly confined to aqueous solutions. Two sets of bulbs are connected in series, the first set containing the solution, the second, solvent only, all being kept at constant temperature. If now a current of dry air is bubbled through the liquids, it will take up an amount of vapour proportional to the vapour tension. From the the first set it will remove a quantity (which can be arrived at by weighing before and after the experiment) proportional to p_1, and from the solvent, which has a higher vapour tension, a further quantity proportional to the difference of vapour tension, $p_0 - p_1$. The total amount removed is proportional to p_0. Hence, by substituting these values, and knowing the concentration of the solution, the molecular weight of the solute can be found.[1]

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[1] Van't Hoff, *K. Svenska Vet.-Akad. Handl.*, 1885, **21**, 38; *Zeitsch. physikal. Chem.*, 1887, **1**, 481; *Phil. Mag.*, 1888, [v.], **26**, 81.

Instead of measuring the depression of vapour tension, it is more usual to determine the elevation of boiling-point which, for dilute solutions, is proportional to it. For, in fig. 67 below, suppose the three curves represent the vapour tension of the solvent I, of a solution II, and of a more concentrated solution III. At a common pressure indicated by the line ABC, the boiling-points are t_1, t_2, and t_3, such that $t_2 - t_1$ (AB) is the elevation for the first solution, and $t_3 - t_1$ (AC) for the second. If dilute solutions only are considered, then the portions of the curves are very short, and may be considered straight and parallel (see p. 114).

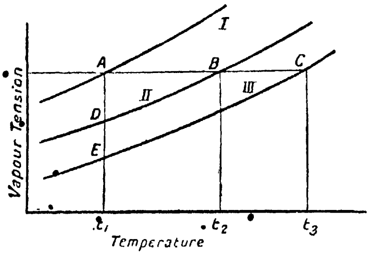

FIG. 67.—Elevation of boiling-point proportional to lowering of vapour tension.

Hence, $$AC : AB = AE : AD,$$

or, the elevation of boiling-point is proportional to the depression of vapour tension.

Rugheimer[2] used a combination of the two processes in determining the molecular weights of a number of metallic chlorides dissolved in molten bismuth chloride. A measurement was first made of the effect of pressure on the boiling-point of the solvent, next, the boiling-point of the solution of known concentration was observed. From the first set of measurements, it was possible to calculate the vapour tension of the pure solvent at the boiling-point of the solution. Hence, also, the depression of the vapour tension at this particular temperature was obtained, and by substituting the values in the equation already given, the molecular weight was found.

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[1] For details, see Ostwald-Luther, *Physiko-chemische Messungen*; Walker, *Zeitsch. physikal. Chem.*, 1888, **2**, 602; Earl of Berkeley and Hartley, *Proc. Roy. Soc.*, 1906, **A**, **77**, 156; *Phil. Trans.*, 1909, **A**, **209**, 177. For other vapour-pressure methods see Biddle, *Amer. Chem. J.*, 1903, **29**, 341; Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 1615.

[2] Rügheimer, *Ber.*, 1903, **36**, 3030; *Annalen*, 1905, **339**, 297; Rügheimer and Rudolfi, *ibid.*, 1905, **339**, 311.

Using the solvent named, Rügheimer and Rudolfi obtained the following results :—

Substance.	Molecular Weight.		Substance.	Molecular Weight.	
	Found.	Calcd.		Found.	Calcd.
LiCl . . .	45·3	42·48	$CaCl_2$ . . .	113·8	111·0
NaCl . . .	65·0	58·5	$SrCl_2$ . . .	163·9	158·55
KCl . . .	70·8	74·6	$BaCl_2$ . . .	203·5	208·3
CsCl . . .	169·5	168·35	$PbCl_2$ . . .	275·2	277·8

Ebullioscopic Methods. The Elevation of the Boiling-Point.

—*Beckmann's Method.*—A convenient form of apparatus for general laboratory use is shown in fig. 68.

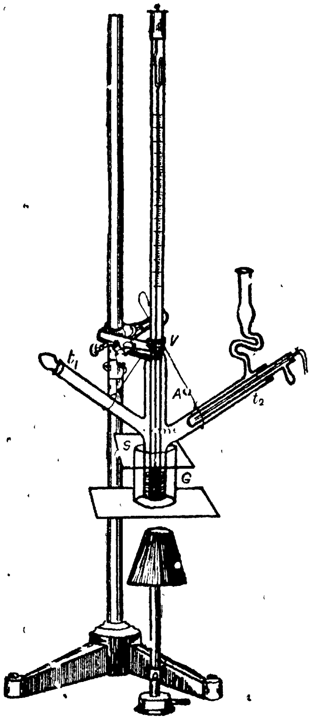

FIG. 68.—Beckmann's boiling-point apparatus.

The boiling-point tube A has two side tubes t_1 and t_2. Through t_1, which is closed by a ground-glass stopper, the substance under investigation is introduced as required. The tube t_2 is longer than t_1, and carries a water condenser to return condensed vapour to the boiling-point tube, and an upright tube containing fused calcium chloride, giving access to the air. A stopper at V carries the Beckmann thermometer which dips into a known weight of the solvent.

The boiling-point tube stands on a square of asbestos millboard, and is protected from cooling effects by surrounding it with a cylindrical glass mantle G containing air, a square of mica, S, cutting off radiant heat and hot air currents from the exposed part of the thermometer. The source of heat is a small gas flame, and superheating is avoided by introducing glass beads, garnets, pieces of granite, or, best of all, small pieces of platinum foil bent into the form of tetrahedra.

The boiling-point of the solvent is first noted. Some little time is generally needed before the temperature becomes steady to within 0·01°. When this condition has been attained, the temperature is noted and the height of the barometer read. The apparatus is allowed to cool a few degrees before the introduction (best in the form of a small pastille) of a known weight of the substance, and afterwards the measurement of boiling-point is repeated with the solution. Several additions of material may be made and readings taken. The boiling-points should be corrected for variations in barometric pressure during the experiment.

The molecular weight is then calculated from a formula very similar to that used for freezing-point measurements, viz.—

$$M = \frac{C \times w}{\Delta \times W},$$

where Δ is now the elevation of the boiling-point, and C is the molecular elevation. The constant C in this equation may, like the corresponding freezing-point constant, be calculated from a theoretical equation, namely,

$$C = \frac{2T^2}{L},$$

where T is the boiling-point (absolute) of the solvent and L its latent heat of vaporisation in calories per gram (see p. 146).

For some common solvents, the following are values of the constant C:—

Benzene	2700	Ethyl alcohol	1170
Chloroform	3900	Acetone	1700
Carbon disulphide	2400	Water	520

The above process gives results which should not vary more than ± 5 per cent.[1]

The Landsberger-Sakurai Method.—Instead of heating the liquid either by a flame or by electrical means, it can be more rapidly raised to its boiling-point by passing in vapour of the solvent. Sakurai[2] first used this method in molecular weight determinations, and the same principle is adopted in the better known Landsberger method.[3] The method, as used by the latter author, was not intended to give results of great accuracy, but the improvements introduced by Turner[4] provide a means of obtaining accurate results at a greater speed than is possible with the ordinary Beckmann apparatus. The latest modification (fig. 69), employed by Turner and Pollard,[5] consists of the molecular weight tube AB, 17·5 cms. in length and 2·8 cms. diameter in the main portion, fitting at a ground glass joint *b* into the boiler CD, which also serves as a constant temperature jacket. Vapour passes from the boiler through E, 12 cms. from the bottom of AB, and issues through two perforations at F into the liquid whose boiling-point is being measured. From the tube AB vapour escapes by the tube KL, which should be as short as possible, into a condenser, connection being made at another ground glass joint *c*. Into the molecular weight tube a ground glass stopper with two tubulures fits at *a*, one tubulure providing the vapour exit, the other an entrance for a short-stemmed Beckmann thermometer of 7–8 mm. diameter.

In carrying out a determination, the molecular weight tube, together with the stopper, vapour exit tube, and thermometer, is weighed to a centigram, and a small but undetermined quantity of solvent then added, a second, and larger quantity being placed in the boiler with two or three pieces of porous pot to produce steady boiling. Vapour passes into the liquid in the molecular weight tube, during which process the tap T_1 is usually kept closed, and by its condensation raises the temperature to the boiling-point, indicated by the constancy of the thermometer reading. Most of the solvent is now returned to the boiler, a known weight of the substance to be tested is placed in the tube, and the process repeated. After reading the temperature, the apparatus is quickly disconnected at *a* and *c*, and the tube, with its attachments and contents, again weighed, T_2 being closed. The weight, less that of the apparatus and solute added, gives the quantity of solvent present. By connecting the apparatus again, and continuing the passage of vapour, a series of readings at different concentrations can be made. It will be noted that in this process the amount of solvent is increased, whereas in the Beckmann method the amount of solvent is fixed, and that of the solute varied as desired.[1]

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[1] For a discussion of the conditions necessary to give accurate results with this method, see Beckmann, *Zeitsch. physikal. Chem.*, 1908, 63, 177.

[2] Sakurai, *Trans. Chem. Soc.*, 1892, 61, 989.

[3] Landsberger, *Ber.*, 1898, 31, 458.

[4] Turner, *Trans. Chem. Soc.*, 1910, 97, 1184.

[5] Turner and Pollard, *Proc. Chem. Soc.*, 1913, 29, 349.

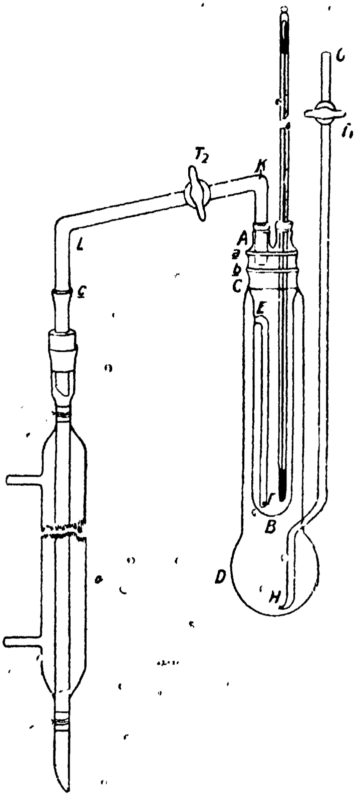

FIG 69.—Turner and Pollard's modification of the Landsberger-Sakurai apparatus.

Molecular Weight by Conductivity Measurements.

—As a result of measurements made on the alkali salts of a large number of acids, Ostwald[2] found the difference in the equivalent conductivities (*vide infra*, p. 205) of N/1024 and N/32 solutions at 25° to be approximately equal to ten times the basicity of the acid. Expressed algebraically—

$$\lambda_{1024} - \lambda_{32} = 10 \times B,$$

where λ_{1024} and λ_{32} are the equivalent conductivities at dilutions of 1024 and 32 litres respectively, and B represents the basicity of the acid.[3]

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[1] For further details, particularly the conditions requisite for accurate measurements, the original papers mentioned above should be consulted.

[2] Ostwald, *Zeitsch. physikal. Chem.*, 1887, **1**, 74; Walden, *ibid.*, 1887, **1**, 529; 1888, **2**, 49.

[3] The rule may be more generally expressed thus:—

$$\lambda_{1024} - \lambda_{32} = n_1 . n_2 . C,$$

where n_1 = valency of anion, n_2 = valency of cation, λ_x = equivalent conductivity at a dilution of x litres per gram-equivalent, and C is a constant for each temperature. At 25° C. the value of the constant is 10.

This rule provides a means of measuring the basicity of an acid and of deciding the formula to be assigned to it and its salts. Thus potassium permanganate was at one time assigned the formula $K_2Mn_2O_8$. The following results prove, however, that the simple formula $KMnO_4$ is the correct one.[1] μ represents the equivalent conductivity, and v the volume of solution, in litres, which contains 1 gram equivalent of solute.

v.	μ.	v.	μ.	v.	μ.
32	113·7	128	119·9	512	122·6
64	117·1	256	121·8	1024	123·7

Whence, $\lambda_{1024} - \lambda_{32} = 10{\cdot}0$.

On the other hand, the simple formula KSO_4 for potassium persulphate was, by the same method, shown to be incorrect, and $K_2S_2O_8$ substituted.[2]

Consideration of Results.—Since, according to Van't Hoff, a substance dissolved in a liquid medium behaves as if it were converted into a gas, it is natural to expect general agreement between the molecular weights of substances in the gaseous state and in solution. Thus, arsenic trichloride dissolved either in benzene[3] or in carbonyl chloride,[4] has the molecular weight corresponding to $AsCl_3$, and the same value is arrived at from vapour density determinations. So, also, iodine is represented by I_2, both in the state of vapour and in solution in bromoform[5] and in a large number of other solvents; and nitrogen peroxide dissolved in acetic acid exhibits the power of forming double molecules to much the same extent as in the state of vapour.[6] Still further, the metals mercury, lead, zinc, and cadmium, which, as vapours, have monatomic molecules, exist in a similar condition in solution in tin.[7]

If different results are found in the two states—and it may be said at once that there are many such cases,—the cause may be traced to one or more of the factors, temperature, concentration, and solvent. With regard to the first, it will be apparent, from the fact that much lower temperatures are used, as a rule, in solution measurements than in vapour, that the possibility of association becomes increasingly greater.

The following are examples of inorganic substances known to be associated in solution in certain solvents: hydrogen chloride and nitrogen peroxide and tri-oxide (in benzene); water; sulphur and phosphorus;[8] antimony trichloride and tribromide; mercuric, zinc, ferric, and lithium chlorides; aluminium bromide and iodide; ammonium, potassium, and rubidium iodides, and the halogen compounds of the organic bases resembling the alkalies. The extent of association varies in practically all cases with concentration, the molecular size increasing as the solution becomes more concentrated, as illustrated by the following examples:—

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[1] Bredig, *Zeitsch. physikal. Chem.*, 1893, **12**, 230.

[2] Walden, *loc. cit.*; Bredig, *loc. cit.*

[3] Raoult, *Compt. rend.*, 1885, **101**, 1056.

[4] Beckmann and Junker, *Zeitsch. anorg. Chem.*, 1907, **55**, 371.

[5] Beckmann and Stock, *Zeitsch. physikal. Chem.*, 1895, **17**, 107.

[6] Ramsay, *Trans. Chem. Soc.*, 1888, **53**, 621.

[7] Heycock and Neville, *Trans. Chem. Soc.*, 1890, **51**, 376.

[8] Beckmann, *Zeitsch. physikal. Chem.*, 1890, **5**, 76.

Phosphorus in Carbon Disulphide.[1]		Antimony Trichloride in Chloroform [2]	
P per 100 grams CS_2.	M. W.	$SbCl_3$ per 100 grams $CHCl_3$.	M. W.
grams.		grams.	
1·581	129	6·4	262
3·723	134	7·34	269
7·44	142	8·88	272
10·84	150	11·1	284
18·86	170		
(P_4=124).		($SbCl_3$=226·6).	

In salts the degree of association depends both on the positive and negative radicle, an increase in the mass of the positive radicle, when a series of similar salts is considered, bringing about a decrease in the degree of association. Thus, in chloroform solutions, each containing 0·025 gram-molecule of solute in 100 grams of solvent, tetraethylammonium bromide has an approximate molecular formula of $[(C_2H_5)_4NBr]_{7·2}$, and tetrapropyl-ammonium bromide $[(C_3H_7)_4NBr)]_{1·76}$. In like manner, ammonium iodide is more strongly associated than potassium iodide, and this, in turn, more than rubidium iodide.[3]

The Influence of the Solvent in Molecular Weight Determinations.—Another factor besides the temperature may serve to make the molecular size in solution different from that in the gaseous state, namely, the influence of the solvent itself. This influence may be chemical or physical, or both. When combination occurs between the solvent and the substance dissolved, it is usually found that the molecular weight of the substance is apparently lowered. Instances of this occur in the determinations made by Werner and his pupils[4] of the molecular weights of a large number of halogen salts of metals, such as CuCl, $AlCl_3$, etc., in piperidine, pyridine, and other solvents, in which combination between solvent and solute occurs.

Where chemical action is absent, the solvent may exert an influence of another kind. Solvents have generally been classed as associating solvents or dissociating solvents according as they allow or prevent the formation, by substances dissolved in them, of aggregates of simple molecules. To the class of so-called associating solvents belong benzene, carbon disulphide, chloroform and bromoform, etc., and to those which prevent association or actually dissociate the molecular complexes of added substances belong water, methyl and ethyl alcohol, and others. It has been shown[5] that the degree of association depends largely on the dielectric constant or specific inductive capacity of the medium, media of high dielectric constant preventing association, whilst those of low value most readily permit of association. A medium of high dielectric constant weakens the attractive forces between molecules, whereas one of low dielectric constant allows these forces freer play, and does not hinder their mutual attractions.[1]

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[1] Beckmann, *loc. cit.*

[2] Turner, *Trans. Chem. Soc.*, 1911, 99, 880.

[3] For references to and discussion of the molecular association of salts, see W. E. S. Turner, *Trans. Chem. Soc.*, 1911, 99, 880.

[4] Werner, *Zeitsch. anorg. Chem.*, 1897, 15, 1.

[5] Turner, *loc. cit.*, also *Trans. Chem. Soc.*, 1912, 101, 1923; Turner and Pollard, *ibid.*, 1914, 105, 1751; Turner and Bissett, 1914, 105, 1777; Meldrum and Turner, *Trans. Chem. Soc.*, 1908, 93 876; 1910, 97, 1605.

The Molecular Formulæ of Inorganic Substances.—From the foregoing it is evident that molecular size, and therefore molecular formula, should be associated with certain definite conditions if any uniform system for writing molecular formulæ is to be obtained. Quantitative knowledge of the molecular state of liquid substances (see this chapter) is at present so uncertain that it is not usual to take it into account in fixing the formulæ to be adopted. Avogadro's Hypothesis is made the basis of the molecular weight system, and equal weight is given to determinations whether made in the state of vapour or solution.[2] No convention has been adopted, however, as to the temperature of comparison, or to the medium to be regarded as the standard. The simplest molecular formula of iodine obtainable is I, not I_2, for dissociation of I_2 begins at as low a temperature as 600°, and at high temperatures the sulphur molecule is undoubtedly represented by S. As to the medium, it is uniformly the same in vapour density determinations, namely, the ether (vacuum), the dielectric constant of which is taken as the standard (and has the lowest) value, unity. For investigation in solution, then, some solvent of low dielectric constant should be used if the process is to be comparable with a vapour density determination, and the state of the free physical molecule is to be ascertained. If water is the solvent, in the case of a salt the simplest possible molecular weight may be no more than a fraction of that corresponding to the simplest chemical formula. It has therefore been suggested by Turner that one of the following schemes be adopted for the derivation of molecular weights and formulæ:—

I. Employ as molecular weights and formulæ those values which actually correspond to the states of the substances under specified conditions.

This means that each substance may be represented by different formulæ according to its temperature and concentration, and also according to the nature of the medium surrounding it.

II. Choose molecular weights and formulæ only from the results of vapour density measurements, as in the original application of Avogadro's Hypothesis, since, by so doing, the medium will be fixed; and use for purposes of comparison temperatures within 100° of the boiling-point.

III. Make vapour density measurements only the basis, and adopt the formulæ corresponding to the highest temperatures attained with the substances.

The first scheme is doubtless the best in theory, but, in the present state of knowledge, hardly possible in practice, and scheme II. is probably better than III. The last-named agrees in some respects with present practice, in that the smallest or simplest possible formula is usually adopted. Thus, H_2, N_2, O_2, $AlCl_3$, NaCl, KCl, AgCl would represent molecules of these substances, as is at present the custom in chemical literature. But then, for the sake of consistency, cuprous chloride should be written Cu_2Cl_2 and not CuCl; and P_2,

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[1] See Turner, *loc. cit.*

[2] The usual custom being to use the smallest possible formulæ obtainable by these processes. See Turner, *Molecular Association* (Longmans, 1915).

As_2, S, I, and from the indications given at 1500°, Br and Cl, should also be written for molecular quantities. Molecular formulæ chosen in accordance with scheme III., however, cannot be regarded as strictly comparable. In any case, whichever of the preceding systems be chosen, the data at present available only suffice for the determination of a limited number of molecular formulæ, and the majority of formulæ can only be regarded as empirical.

Abnormal Molecular Weights in Aqueous Solution. The Theory of Electrolytic Dissociation.—When water is the solvent[1] in molecular weight determinations and the substances concerned are electrolytes—acids, bases, or salts,—the results differ essentially from those observed with non-electrolytes, such as cane sugar, urea, etc. Molecule for molecule, an electrolyte always produces a greater osmotic pressure or depression of freezing-point than a non-electrolyte. Accordingly, at the time when Van't Hoff showed, from his interpretation of Pfeffer's osmotic pressure measurements, that the equation $PV = RT$ holds alike for gases and solutions, he was obliged to introduce into the equation, where electrolytes were concerned, a factor i (the so-called Van't Hoff's factor),

$$\text{where } i = \frac{\text{Obs. osmotic pressure}}{\text{Calcd. osmotic pressure}} \text{ or } \frac{\text{Obs. F.Pt. depression}}{\text{Calcd. F.Pt. depression}},$$

the solution being of normal concentration. For salt solutions of this strength, accordingly, the gas equation became $PV = iRT$.

The explanation of this phenomenon, put forward by Arrhenius in 1887, is known as the Theory of Electrolytic Dissociation or the Ionic Theory. It will receive detailed treatment in a subsequent chapter (see Chap. VI.).

THE MOLECULAR WEIGHTS OF PURE LIQUIDS.

Many methods have been proposed by which the molecular weight of a liquid substance may be measured, but none of them possesses a sound theoretical basis such as Avogadro's hypothesis affords to the study of gases and dissolved substances. At best, the results can only be regarded as approximate. Of the various methods, only those which have in some measure been used with inorganic substances are discussed.

Ramsay and Shields' Method. — The early work of Eötvös[2] formed the basis upon which Ramsay and Shields[3] founded a method for determining the molecular weights of pure substances in the liquid state.

It has been seen in Chapter II. that if P, V, and T denote the pressure, gram-molecular volume, and absolute temperature of a gas, then

$$PV = RT,$$

where R is a constant, independent of the nature of the gas. The product PV may be termed the volume-energy of the gas. An equation of similar type has been shown to hold, within certain limits, between the surface-energy of a liquid and the temperature. The equation is

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[1] Turner and his co-workers have shown that the molecular weight of a solute is almost entirely a function of the dielectric constant of the solvent. When this constant is high, the molecular weights of electrolytic solutes are smaller. Water, formic acid, formamide, and hydrogen cyanide—all solvents of high dielectric constant—behave similarly. Thus water is not really abnormal in its behaviour although, being the first case of its kind to be studied, it was regarded as exceptional.

[2] Eotvos, *Wied. Annalen*, 1886, 27, 448.

[3] Ramsay and Shields, *Phil. Trans.*, 1893, **A**, 184, 647; *Trans. Chem. Soc.*, 1893, 63, 1089.

$$\gamma . s = k\,\tau,$$

where $(\gamma . s)$ is the surface energy, τ the temperature measured downwards from the critical temperature, and k is a constant, independent of the nature of the liquid. The surface energy is the product of γ, the surface tension between the liquid and its vapour, and s, which denotes a surface over which are distributed a certain definite number of molecules the same for all liquids.

The preceding equation was found by Ramsay and Shields to be only approximately true. The relationship between $(\gamma . s)$ and τ was found to be as indicated in fig. 70, the portion OC of the graph starting from the critical temperature at O being curved, and the portion CA being rectilinear. Hence it is necessary to subtract from τ the value $OB = d$, say, and not to use the equation at temperatures between D and O. The corrected equation is therefore

$$\gamma . s = k(\tau - d).$$

The value of d is usually about 6.

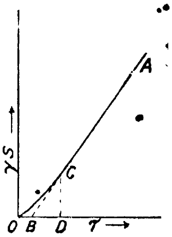

FIG. 70.—Variation of molecular surface energy with the temperature.

As a measure of s, the expression $(Mv)^{\frac{2}{3}}$, proposed by Eotvos, is adopted; M and v denote the molecular weight and specific volume (*i.e.* volume occupied by one gram) of the liquid, respectively.

In order to eliminate d and arrive at the value of k, measurements of specific volume and surface tension are made at two different temperatures. Denoting simultaneous values by the same suffix, the equations

$$\gamma_1(Mv_1)^{\frac{2}{3}} = k(\tau_1 - d)$$
$$\gamma_2(Mv_2)^{\frac{2}{3}} = k(\tau_2 - d)$$

lead to the following equation for k:—

$$k = \frac{\gamma_1(Mv_1)^{\frac{2}{3}} - \gamma_2(Mv_2)^{\frac{2}{3}}}{(\tau_1 - \tau_2)}.$$

Now it is found that if k be determined from this equation, using for M the molecular weight of the substance in the gaseous state, the value is 2·12 (using C.G.S. units) for quite a number of substances. It is therefore concluded that these substances undergo no change in molecular weight on their passage from the gaseous to the liquid state.[1] Among such *normal liquids* are benzene, chlorobenzene, and ether. When, therefore, it is observed that the value of k for a liquid is less than 2·12, it is concluded that association takes place when the vapour condenses to liquid (since to obtain the normal value of k a greater value for M is necessary than the one that has been assumed). From the observed value of k_1 for any particular substance, it is possible to derive an approximate measure of the *degree of association*. Thus, if association has taken place, k_1 is less than 2·12, simply because the mass of the molecule is not truly represented by M, but by xM, where x greater than unity and expresses the degree of association. Hence, whilst

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[1] For a discussion of this point, see Young, *Stoichiometry* (Longmans, 1918), pp. 222 and 352.

$$\gamma(\mathrm{M}v)^{\frac{2}{3}} = k_1(\tau - d),$$

by substituting xM for M the equation becomes

$$\gamma(x\mathrm{M}v)^{\frac{2}{3}} = 2{\cdot}12(\tau - d),$$

whence

$$x = (2{\cdot}12/k_1)^{\frac{3}{2}}$$

approximately.

The practice of the method requires the determinations at two temperatures (for accuracy, not less than 10° apart) of surface tension and density. The surface tension is measured by the height to which the liquid rises in a capillary tube, and is calculated from the equation $\gamma = gr\sigma h/2$, where h is the height of liquid, σ the density, r the radius of the tube at the meniscus of the liquid, and g the constant of gravitation. From the density the specific volume v is obtained, since $v = 1/\sigma$.[1]

The following table, compiled from the results of several investigations,[2] records the degree of association of a number of substances:—

Substance.	Temperature °C.	x.	Substance.	Temperature °C	x.
Phosphorus trichloride .	16–46	1·02	Sulphuric acid . .	10·2–132·5	32·3
Sulphur monochloride .	46–78	1·01	Sodium nitrate. .	330–400	10·7
Sulphuryl chloride .	16–46	0·97	Potassium nitrate .	,,	8·7
Silicon tetrachloride .	18·9–45·5	1·06	Silver chloride . .	...	3·29
Hydrogen chloride . .	159–192 abs.	1·72	Lead chloride . .	..	3·60
Water	20–30	3·81			

Ramsay and Shields' method has been employed much more than any other for determining the molecular weights of liquids, but in a number of cases the value of k is considerably greater than 2·12, which would apparently represent a state of dissociation of the molecule. In most instances where this is observed there is no reason to believe that dissociation actually occurs, and the existence of such cases shows that implicit reliance cannot be placed upon the method.[3] It is more reliable to regard a liquid as normal when $(\gamma . s)$ is a linear function of the temperature than to judge by the numerical value of k.

The surface tension of the liquid need not be measured by the *capillary tube* method. Morgan uses the *drop-weight* method, basing it upon Tate's

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[1] For details of apparatus and methods, see Ramsay and Shields, *loc. cit.*; Dutoit and Friderich, *Arch. Sci. phys. nat.*, 1900, [iv.], **9**, 105; Guye and Baud, *ibid.*, 1900, [iv.], **11**, 409, 537; Hewitt and Winmill, *Trans. Chem. Soc.*, 1907, **91**, 441; Renard and Guye, *J. Chim. phys.*, 1907, **5**, 81.

[2] Ramsay and Shields, *loc. cit.*; Ramsay and Aston, *Trans. Chem. Soc.*, 1894, **65**, 167; Bottomley, *ibid.*, 1903, **83**, 1421; Lorenz and Kaufler, *Ber.*, 1908, **41**, 3727.

[3] See Dutoit and Friderich, *loc. cit.*; Miss Homfray and Guye, *J. Chim. phys.*, 1903, **1**, 505; Turner and Merry, *Trans. Chem. Soc.*, 1910, **97**, 2069; Walden, *Zeitsch. physikal. Chem.*, 1910, **75**, 555; Tyrer, *ibid.*, 1912, **80**, 50; Guye, *J. Chim. phys.*, 1911, **9**, 505; Walden and Swinne, *Zeitsch. physikal. Chem.*, 1912, **79**, 700; 1913, **82**, 271.

Law that the weight of a drop of liquid, formed at the plane end of a thick-walled tube of capillary bore and allowed to fall as the result of its own weight, is proportional to the diameter of the end of the tube and to the surface tension of the liquid.[1] Tate's Law, however, is only approximately true under certain conditions, as has been shown theoretically by Lohnstein and practically by Harkins and Humphrey. The latter investigators have shown that the drop-weight method may be accurately applied without assuming Tate's Law.

Trouton's Law.[2]—Trouton's Law, usually stated in mathematical form, is ML/T = constant, where M is the molecular weight of the substance (as a gas), L its latent heat of evaporation, and T the temperature of the boiling-point (at atmospheric pressure) measured on the absolute scale.

Walden, from a large number of measurements with normal liquids, gives 20·7 as the value of the constant for normal liquids. If the observed value is appreciably higher than this, it is taken as indicating association of the molecules during passage from the gaseous to the liquid state. Thus, liquid ammonia gives the value 23·6 and water about 26, so that these substances in the liquid state are not represented by the simple formulæ NH_3 and H_2O respectively, as indeed all methods agree in indicating.

Walden's Methods.—Walden has deduced a method in which the surface tension is involved, but which differs essentially from the Ramsay and Shields' method. The surface tension results are not employed in the ordinary units, but in terms of the *specific cohesion* $a^2 = 2\gamma/\sigma$, where γ is the surface tension and σ the density. Walden[3] finds that between the latent heat of evaporation and the specific cohesion, when both are measured at the boiling-point, a relationship exists such that L/a^2 = constant. The average value of the constant is found to be 17·9. But, according to Trouton's Law, ML/T = 20·7. By substituting the value $L = 17{\cdot}9a^2$ in this equation, the expression $M = 1{\cdot}16T/a^2$ is obtained, whereby the molecular weight of the liquid can be calculated.

By this method Walden found, for instance, that $SnCl_4$, $SiCl_4$, Br_2, CCl_4, PCl_3, SO_2Cl_2, and CS_2 were the formulæ actually representing these substances in the liquid state. Furthermore, the anomalous results found with certain compounds when Ramsay and Shields' process is adopted are not found with this method.

A slight modification of this process has been applied by Walden to many inorganic substances, particularly salts. Substances at their boiling-points are at approximately comparable temperatures, for, very roughly, the boiling-point temperature is two-thirds of the critical value, both measured on the absolute scale. If the melting-points of substances could be similarly regarded as comparable temperatures, then the expressions L/a^2 and ML/T would also be constant at the melting-point. Therefore, in turn, the expression $M = (\text{constant}) \times T/a^2$ would be applicable at the melting-point (T), although the constant would have a different value from the preceding.

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[1] Morgan and Stevenson, *J. Amer. Chem. Soc.*, 1908, **30**, 360; Morgan and Higgins, *ibid.*, 1908, **30**, 1055; Morgan, *ibid.*, 1911, **33**, 349 and 643; Morgan and Thomssen, *ibid.*, 1911, **33**, 657; and numerous other subsequent papers in the same journal. See also Lohnstein, *Ann. Physik*, 1906 [iv.], **20**, 237, 606; *Zeitsch. physikal. Chem.*, 1908, **64**, 686; 1913, **84**, 410; Harkins and Humphrey, *J. Amer. Chem. Soc.*, 1916, **38**, 228, 236, 242; Harkins and Brown, *ibid.*, p. 246. Reference should also be made to the work of Jaeger and his co-workers (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 329, and subsequent papers), in which the pressure within an immersed gas bubble on the point of bursting is utilised to measure the surface tension of the liquids.

[2] For the derivation of this law see Young, *Stoichiometry* (Longmans, 1908), p. 155.

[3] Walden, *Zeitsch. physikal. Chem.*, 1909, **65**, 129, 257, 547; Kistiakowsky, *Zeitsch. Elektrochem.*, 1906, **12**, 513; Dutoit and Mojoiu, *J. Chim. phys.*, 1909, **7**, 169.

Walden tested this expression for measurements made at the melting-point and found, for a large number of non-associated liquids, that Ma^2/T is actually a constant and equal to 3·65. Hence the molecular weight of a liquid at its freezing-point is obtainable from the equation $M = 3{\cdot}65T/a^2$. The results all indicate that fused salts have very complex molecules, the degree of complexity of sodium chloride being 10; sodium bromide 8; sodium iodide 6·2. In all the cases investigated, the chloride is most and the iodide least associated.

Of other methods which have been proposed, special reference may be made to that of Guye.[1] This investigator points out that the presence, even to a small extent, of associated vapour molecules, is an indication of extensive association in the liquid state. In both states there is an equilibrium, depending on the temperature, between the various forms of the substance present. From the known concentrations of these in the vapour (see p. 141), and the known volume of vapour produced from unit volume of liquid, Guye calculates the degree of association in the liquid state. At present the method has only been applied to water, and the results indicate that in the liquid state water consists of a mixture of $(H_2O)_3$, $(H_2O)_2$, and H_2O, called respectively trihydrol, dihydrol, and hydrol. These results are in general agreement with the views of Bousfield and Lowry,[2] and partly also with those of Sutherland[3] and of Armstrong.[4]

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[1] Guye, *Trans. Faraday Soc.*, 1910, **6**, 78.

[2] Bousfield and Lowry, *Trans. Faraday Soc.*, 1910, **6**, 15.

[3] Sutherland, *Phil. Mag.*, 1900, [v.], 50, 460; *Trans. Faraday Soc.*, 1910, **6**, 105.

[4] H. E. Armstrong, *Proc. Roy. Soc.*, 1908, **A**, **81**, 80.

CHAPTER V.

CHEMICAL CHANGE.

Types of Chemical Change.—A general idea of the nature of chemical change and its distinction from physical change has been given in Chapter I. The further consideration of chemical change will form the subject of the present chapter.

The following types of chemical change may be recognised:—

1. *Combination*—Two or more substances unite to form one new substance. Examples are (*a*) the union of mercury and oxygen to form mercuric oxide; (*b*) the union of hydrogen and chlorine to form hydrogen chloride; (*c*) the union of phosphorus trichloride and chlorine to form phosphorus pentachloride; (*d*) the union of sulphur trioxide and water to form sulphuric acid, etc.:—

$$\begin{aligned}
&(a)\ 2Hg + O_2 &&= 2HgO\\
&(b)\ H_2 + Cl_2 &&= 2HCl\\
&(c)\ PCl_3 + Cl_2 &&= PCl_5\\
&(d)\ SO_3 + H_2O &&= H_2SO_4.
\end{aligned}$$

The addition of oxygen to a substance is termed *oxidation*; the addition of hydrogen, *reduction*.[1] Thus (*a*) and (*b*) represent the oxidation of mercury and the reduction of chlorine respectively. A substance is said to be *synthesised* from its elements when it is formed by the direct union of its constituent elements, and accordingly (*a*) and (*b*) denote the synthesis of mercuric oxide and hydrogen chloride respectively.[2]

2. *Decomposition* of a substance into two or more simpler substances. Examples are (*a*) the decomposition of calcium carbonate into carbon dioxide and calcium oxide; (*b*) of phosphorus pentachloride into phosphorus trichloride and chlorine; (*c*) of ammonium nitrate into nitrous oxide and water, etc., all of which are effected by the application of heat:—

$$\begin{aligned}
&(a)\ CaCO_3 &&= CaO + CO_2\\
&(b)\ PCl_5 &&= PCl_3 + Cl_2\\
&(c)\ NH_4NO_3 &&= N_2O + 2H_2O.
\end{aligned}$$

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[1] *Oxidation* also comprises subtraction of hydrogen, the increasing of electro-negative atoms or radicles in a molecule, and the diminution of electro-positive atoms or radicles in a molecule; *reduction* also comprises subtraction of oxygen, the increasing of electro-positive atoms or radicles in a molecule and the diminution of electro-negative atoms or radicles in a molecule.

[2] The building up of a substance from its elements, even when it is necessary to perform the process in a number of stages, is also termed its *synthesis*.

3. *Dissociation.*—It will be noticed that one of the reactions described above as a combination is also described as a decomposition. This apparent contradiction arises from the fact that according to the conditions of the experiment, the reaction can be made to proceed in either direction. It is accordingly a reversible reaction. *Reversible decomposition* is known as *dissociation.* The fact that a reaction is reversible is indicated by replacing the sign of equality in the chemical equation by $\rightleftharpoons$;[1] so that the preceding dissociation is written:—

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2.$$

Reversible reactions in general will be discussed later.

4. *Displacement* of one element in a compound by the action of another element. Examples are (*a*) the displacement of hydrogen in hydrogen chloride by zinc; (*b*) of iodine in hydrogen iodide by chlorine; (*c*) of iron in ferric oxide by hydrogen; (*d*) of silver in silver sulphate by copper, etc.:—

$$\begin{aligned}
&(a)\ Zn &&+ 2HCl &&= ZnCl_2 &&+ H_2\\
&(b)\ 2HI &&+ Cl_2 &&= 2HCl &&+ I_2\\
&(c)\ Fe_2O_3 &&+ 3H_2 &&= 2Fe &&+ 3H_2O\\
&(d)\ Ag_2SO_4 &&+ Cu &&= CuSO_4 &&+ 2Ag.
\end{aligned}$$

Such a displacement as (*c*) is a *reduction*, viz. the reduction of iron oxide to iron by removal of oxygen. Similarly, the removal of hydrogen from hydrogen iodide in (*b*) is an *oxidation* of hydrogen iodide to iodine.

5. *Double decomposition* or *metathesis.*—This type is of very frequent occurrence, and may be represented generally as follows:—

$$AB + CD = AC + BD.$$

Examples are (*a*) the interaction of hydrogen chloride and silver nitrate; (*b*) of barium nitrate and sodium sulphate; (*c*) of sodium chloride and sulphuric acid, etc.:—

$$\begin{aligned}
&(a)\ HCl &&+ AgNO_3 &&= AgCl &&+ HNO_3\\
&(b)\ Ba(NO_3)_2 &&+ Na_2SO_4 &&= 2NaNO_3 &&+ BaSO_4\\
&(c)\ NaCl &&+ H_2SO_4 &&= NaHSO_4 &&+ HCl.
\end{aligned}$$

Double decomposition in which water is one of the starting materials, is called *hydrolysis*, or *hydrolytic decomposition*; *e.g.* the decomposition of phosphorus tribromide by water:—

$$PBr_3 + 3H_2O = H_3PO_3 + 3HBr.$$

6. *Substitution.*—This somewhat resembles displacement, but the displaced element combines with the displacing element. For example, the first action of chlorine on methane is represented thus—

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$

Substitution is of frequent occurrence in organic chemistry.

The preceding are the simpler types of chemical change. The classification here employed is independent of chemical theory. Frequently, however, the classification of chemical reactions is based upon the molecular and atomic theories, when the results differ somewhat from the preceding. For instance, the synthesis of hydrogen chloride is then looked upon as a double decomposition—

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[1] This symbol, proposed by H. Marshall, is more commodious than $\rightleftarrows$, which is frequently employed.

$$HH + ClCl = HCl + HCl.$$

Further, the term "dissociation" is restricted to mean the reversible decomposition of one molecule into several others. This restriction, however, is not adhered to in practice, the decomposition of calcium carbonate being almost invariably called a dissociation, although the molecular weight of calcium carbonate is unknown.

In the present state of knowledge concerning molecular weights, it is impossible to carry out a classification based upon molecular considerations without having to assume the molecular formulæ of a large number of substances.

There is another type of change which differs markedly from the preceding, viz. that in which one substance is quantitatively transformed into another, without either the addition or the subtraction of any material substance. Thus the change is not associated with any change in composition. Examples are the conversion of yellow into red phosphorus, of oxygen into ozone (see allotropy, p. 64), the transformation of ammonium cyanate into urea, etc.[1] Such changes are called *internal rearrangements*, and are attributed to rearrangements of the atoms in the molecules. It is when such reactions as these are considered that the separation of chemical from physical changes becomes difficult, for there is a close resemblance between the changes quoted above and the changes of the nature of fusion, evaporation, transition from one crystalline form to another, etc. (see Chap. II.), which are usually classed as physical changes.

THERMOCHEMISTRY.

Introductory.—It has been already stated (p. 5) that a chemical change is accompanied by an evolution or absorption of heat, this being the usual manner in which the difference between the internal energy of the system in its initial and final states is rendered evident. Since, however, many physical changes—fusion, vaporisation, etc.—are attended by thermal changes, this phenomenon alone does not distinguish between chemical and physical change. The study of the thermal effects associated with chemical changes is termed *thermochemistry*.[2]

Thermochemical change is readily understood in the light of the law of conservation of energy (p. 5). Each substance under given conditions possesses a definite amount of internal energy, usually termed its *intrinsic energy*. The sum of the intrinsic energies of the various substances which undergo change is, in general, different from the sum of the intrinsic energies of the substances produced. The difference, expressed in heat units,

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[1] *Dissociations* such as the following—

$$N_2O_4 \rightleftharpoons 2NO_2,$$
$$I_2 \rightleftharpoons 2I$$

are also changes in which there is no alteration in composition.

[2] For further information the reader is referred to the following works: Thomsen, *Thermo-chemistry*, translated by Burke (Longmans & Co., 1908); Muir and Wilson, *Elements of Thermal Chemistry* (Macmillan & Co., 1885); Ostwald, *Lehrbuch der allgemeinen Chemie* (Leipzig, 2nd edition, 1893), vol. ii., pt. 1, and the works of Thomsen and Berthelot referred to later.

is called the *heat tone* of the reaction; when it represents heat liberated, the reaction is said to be *exothermic*, whilst when heat is absorbed, the reaction is described as *endothermic*. The majority of reactions are exothermic. The heat tone of a reaction is usually accounted for as the thermal change observed, but in certain circumstances it may appear partly as electrical energy, sound, etc., whilst there is frequently external work done on or by the system. It is only possible to determine the *difference* between the intrinsic energies of two systems, one of which may be converted into the other, and thermochemical measurements afford the easiest means of acquiring such data. The reactions chosen for these measurements are those, like solution, dilution, neutralisation, etc., which can be quickly effected at ordinary temperatures and in which the only energy changes to be considered are those due to thermal change and external work. In such reactions the observed heat of reaction practically coincides with the heat tone when solids and liquids only are concerned, the external work being negligible. When gases are produced or used up, a small correction is necessary to obtain the heat tone of the reaction.[1]

Historical.—The first important generalisation discovered in thermochemistry is due to Lavoisier and Laplace;[2] namely, that the quantity of heat required to decompose a compound into its elements is equal to the heat evolved when the compound is formed from its elements. The father of modern thermochemistry, however, is Hess, whose work appeared in 1840.[3] Hess discovered the fundamental law upon which all thermochemical calculations are based. This law, known as the *Law of Constant Heat Summation*, may be stated as follows:—

The heat developed in a chemical change depends only on the initial and final stages of the system, and is independent of the intermediate stages through which the system passes.[4]

For example, the total heat developed when a quantity of ammonia gas is allowed to react with its equivalent of hydrogen chloride and the product dissolved in a large quantity of water is equal to that developed when the same quantities of these substances are separately dissolved in excess of water and the two solutions mixed. Hess arrived at the law by experiment some years before the law of the conservation of energy was recognised. Subsequently J. Thomsen pointed out that Hess's Law could be deduced from the law of conservation of energy.

Most thermochemical measurements have been carried out by two chemists and their pupils. The experimental work of J. Thomsen commenced in 1853, that of M. Berthelot in 1873. Throughout their lives, these two investigators were constantly occupied with thermochemical problems, and they accumulated a vast amount of data of considerable accuracy.[5] The pioneering work of Favre and Silbermann,[1] and the later work of Stohmann[2] should also be mentioned. The revision of a large amount of thermochemical data has been commenced by T. W. Richards, and a number of results have been already published.[3]

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[1] This amounts to 0·58 Cal. per gram molecule of gas at 18° (*vide supra*, p. 28). To obtain the heat tone, it is added to the heat measured calorimetrically for each gram molecule of gas produced (since its equivalent has been expended in work done *by* the system), and subtracted for each gram-molecule of gas that disappears (since its equivalent in heat is developed from work done *on* the system). In the examples given the values denote heat tones.

[2] Lavoisier, *Œuvres*, vol. ii. p. 287.

[3] Hess, *Pogg. Annalen*, 1840, **50**, 385; Ostwald's *Klassiker*, No. 9.

[4] It is, of course, understood that the production of electrical energy, sound, etc., is not supposed to occur.

[5] Published in the following works: Thomsen, *Thermochemische Untersuchungen* (Leipzig, 1882-6), 4 vols.; Berthelot, *Essai de méchanique chimique fondée sur la thermochimie* (Paris, 1879), and *Thermochimie donnécs et lois numériques* (Paris, 1897), 2 vols.

Thermochemical Methods, Notation, etc.—The practice of thermochemistry belongs to the branch of physics known as calorimetry and cannot be described here.[4] Such reactions as solution, neutralisation, etc., are carried out in an ordinary open calorimeter, but the heats of combustion of substances are measured by means of a calorimetric bomb, a closed steel vessel lined with platinum or enamel, in which the substance is burned in oxygen under several atmospheres pressure. The substance is placed in contact with a wire heated electrically to start the reaction, and the heat liberated is determined by submerging the bomb in a known mass of water and observing the rise in temperature.

There are three units of heat in common use in terms of which the results are usually stated, namely, the gram-calorie at 18°, written *cal.*, the kilogram-calorie, which equals one thousand gram-calories and is written *Cal.*, and the heat required to raise the temperature of one gram of water from 0° to 100° is adopted as the unit. The latter is practically one hundred gram-calories, and is written K.[5]

The simplest method of expressing the *heat of reaction* corresponding to a change is to write down the change in the customary way as an equation, and affix the magnitude of the thermal effect at the end, a positive sign indicating heat evolution, a negative one heat absorption. The quantity of heat stated is that corresponding to the reaction between the number of formula weights expressed in the equation, the unit of mass being the gram. For example, the equation

$$[\mathrm{Zn}] + (\mathrm{Cl}_2) = [\mathrm{ZnCl}_2] + 97\cdot2 \text{ Cals.}$$

indicates that when 65·37 grams of zinc unite with 70·92 grams of chlorine, 97·2 Cals. of heat are evolved.

When a substance is dissolved in a large excess of water, the further addition of water has no thermal effect. To indicate that a substance is dissolved in such an excess of water, the abbreviation Aq is appended to its formula. For example, the equation

$$[\mathrm{ZnCl}_2] + \mathrm{Aq.} = \mathrm{ZnCl}_2.\mathrm{Aq.} + 15\cdot6 \text{ Cals.}$$

means that the solution of 136·29 grams of zinc chloride in a large excess of water is attended with the evolution of 15·6 Cals., whilst the equation

$$\mathrm{HCl.Aq.} + \mathrm{NaOH.Aq.} = \mathrm{NaCl.Aq.} + 13\cdot7 \text{ Cals.}$$

denotes that when 36·47 grams of hydrogen chloride in dilute aqueous solution are mixed with 40·01 grms. of sodium hydroxide in dilute aqueous solution, the production of a solution of sodium chloride is attended with the evolution of 13·7 Cals. If necessary, the precise amount of water used may be indicated, as in the following example :—

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[1] Favre and Silbermann, *Ann. Chim. Phys.*, 1852, [iii.], **34**, 357; 1852, [iii.], **36**, 1; 1853, [iii.], **37**, 406.

[2] Stohmann, *J. prakt. Chem.*, 1889, **39**, 503.

[3] Richards, *J. Amer. Chem. Soc.*, 1909, **31**, 1275; Richards and Jesse, *ibid.*, 1910, **32**, 268; 1914, **36**, 248; Richards and Burgess, *ibid.*, 1910, **32**, 431, Richards, Rowe, and Burgess, *ibid.*, 1910, **32**, 1176; Richards and Rowe, *Zeitsch. physikal. Chem.*, 1913, **84**, 585.

[4] For details see the works already quoted, and standard works on heat

[5] The definition of the unit of heat is discussed on p. 86; the precise temperature at which the calorie is defined does not really matter as far as most thermochemical results are concerned, since they are not yet known with great precision.

$$[Zn] + 2HCl.200H_2O = ZnCl_2.400H_2O + (H_2) + 36{\cdot}6 \text{ Cals.}$$

It is usual to denote the state of aggregation of each substance, for which purpose, as indicated in the preceding examples, the formulæ of solids are enclosed in square brackets (or printed in heavy type) and those of gases in round brackets, liquids and solutions having no brackets. This should always be done when ambiguity might otherwise arise.

Unless the contrary is stated, the differences in intrinsic energies expressed in these equations hold good for the substances concerned at 18°. This is so with the examples already given. The heat of reaction varies with the temperature, for the intrinsic energies of the initial and final systems are increased by rise of temperature, but not, in general, at the same rate. If the heat of reaction at t_1° C. is equal to q, and the mean thermal capacities of the initial and final systems between t_1° and t_2° are s_1 and s_2 respectively, then the heat of reaction at t_2° is obviously equal to $q + (s_1 - s_2)(t_2 - t_1)$. Should any change of state occur between t_1 and t_2, the latent heat of change of state must clearly be taken into consideration.

The difference, expressed in heat units, between the internal energy of the formula-weight in grams of a compound and the sum of the internal energies of its constituent elements in the free state is called the *heat of formation* of the compound. The heat of formation of the compound $A_xB_yC_z$ . . . is therefore the thermal effect q of the reaction

$$xA + yB + zC + \ . \ . \ . = A_xB_yC_z \ . \ . \ . + q \text{ Cals.};$$

for example,

$$[C] + 2[S] = CS_2 - 19{\cdot}6 \text{ Cals.}$$

In general, such equations do not represent reactions which can be directly effected, and their thermal values are obtained indirectly by means of Hess's Law. A compound is said to be *exothermic* or *endothermic* according as q denotes heat evolution or heat absorption. Thus, carbon disulphide is endothermic, its heat of formation being − 19·6 Cals.

The notation already explained is due to Ostwald. Thomsen's method is shorter, but the states of aggregation are not indicated by it. The formulæ of the reacting substances are written down side by side and separated by commas; the whole is enclosed in a square bracket and the products of the reaction are not indicated.[1] The preceding examples become :—

$$[Zn, Cl^2] = 97{\cdot}2 \text{ Cals.}; \qquad [ZnCl^2, Aq] = 15{\cdot}6 \text{ Cals.};$$

$$[HCl.Aq., NaOH.Aq.] = 13{\cdot}7 \text{ Cals}; \qquad [Zn, 2HCl.200H_2O] = 36{\cdot}6 \text{ Cals.};$$

$$[A^x, B^y, C^z \ . \ . \ .] = q; \qquad [C, S^2] = -19{\cdot}6 \text{ Cals.}$$

Heats of Formation.—It has been already stated that heats of formation are usually obtained indirectly. Two simple examples must here suffice to illustrate the method; the principle is the same even in the most complex calculations.

It is not possible to determine directly the heat of formation of carbon monoxide, but the desired result is readily deduced from the following experimental data:—

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[1] For another system of notation, see Pollok, *Seventh Internat. Congress Appl. Chem.*, 1909, Section X., p. 63.

$$[C] + (O_2) = (CO_2) + 96{\cdot}96 \text{ Cals.} \quad \text{(i.)}$$
$$(CO) + (O) = (CO_2) + 67{\cdot}67 \text{ Cals.} \quad \text{(ii.)}$$

If the required heat of formation of the monoxide be x, then by Hess's Law (p. 162),

$$x + 67{\cdot}67 = 96{\cdot}96$$
$$\therefore \quad x = 28{\cdot}29 \text{ Cals.}$$

In fact, the thermal equations may be subjected to the usual algebraic processes, and the desired result follows immediately by subtracting (ii.) from (i.):—

$$[C] + (O) - (CO) = 28{\cdot}29 \text{ Cals.}$$

or

$$[C] + (O) = (CO) + 28{\cdot}29 \text{ Cals.}$$

The heat of formation of carbon disulphide, impossible to measure directly, follows easily from the following experimental data:—

$$CS_2 + 3(O_2) = (CO_2) + 2(SO_2) + 258{\cdot}73 \text{ Cals.} \quad \text{(i.)}$$
$$[C] + (O_2) = (CO_2) + 96{\cdot}96 \text{ Cals.} \quad \text{(ii.)}$$
$$2[S] + 2(O_2) = 2(SO_2) + 142{\cdot}16 \text{ Cals.} \quad \text{(iii.)}$$

Adding (ii.) and (iii.) and subtracting (i.) from the result,

$$[C] + 2[S] - CS_2 = -19{\cdot}61 \text{ Cals.}$$

i.e.

$$[C] + 2[S] = CS_2 - 19{\cdot}61 \text{ Cals.}$$

The preceding examples serve to illustrate another point. When an element occurs in allotropic forms, or a compound in more than one crystalline form, it is necessary to state which form is used, since the various forms differ in their intrinsic energies. The magnitudes of these differences are not difficult to calculate; for instance—

$$\underset{\text{amorphous}}{[C]} + (O_2) = (CO_2) + 96{\cdot}96 \text{ Cals.}$$

$$\underset{\text{graphite}}{[C]} + (O_2) = (CO_2) + 93{\cdot}36 \text{ Cals.}$$

subtracting

$$\underset{\text{amorphous}}{[C]} - \underset{\text{graphite}}{[C]} = 3{\cdot}6 \text{ Cals.}$$

The preceding data refer to amorphous carbon and rhombic sulphur.

The heats of formation of a large number of compounds have been calculated.[1] They are of great use, since they enable heats of reaction to be calculated. The simple rule is this: replace each formula in the chemical equation by the heat of formation of the compound with the sign changed. For instance, take the reaction

$$3PbS + 2Al = Al_2S_3 + 3Pb + x \text{ Cals.}$$

The heats of formation of lead sulphide and aluminium sulphide are 18·3 Cals. and 122·4 Cals. respectively; of aluminum and lead, zero. Hence

$$-3 \times 18{\cdot}3 + 0 = -122{\cdot}4 + 0$$
$$x = 67{\cdot}5 \text{ Cals.}$$

---

[1] Tables of data are to be found in Ostwald, *opus cit.*, Thomsen-Burke, *opus cit.*, etc.

If, instead of using the rule, the calculation is made in full, it is as follows:—

$$2[Al] + 3[S] = [Al_2S_3] + 122{\cdot}4 \text{ Cals.}$$
$$3[Pb] + 3[S] = 3[PbS] + 54{\cdot}9 \text{ Cals.}$$

Subtracting $$2[Al] - 3[Pb] = [Al_2S_3] - 3[PbS] + 67{\cdot}5 \text{ Cals.}$$

i.e. $$3[PbS] + 2[Al] = [Al_2S_3] + 3[Pb] + 67{\cdot}5 \text{ Cals.}$$

Heats of Solution.—When a gram-molecule of a solute A is dissolved in *a* gram-molecules of water to form a saturated solution, the heat tone q_a of the reaction

$$[A, aH_2O] = q_a$$

is called the *integral heat of solution* of A. If more solvent than this be employed, say xH_2O, the heat tone q_x will be different, but as x is further and further increased, the value of q_x approaches a limit, since the further dilution of an already dilute solution has very little thermal effect. This limiting value, the heat of dilute solution q_∞,

$$[A, \infty H_2O] = q_\infty$$

is what is usually understood by the term *heat of solution.*

When the solution AxH_2O is diluted with an indefinitely large amount of water, the heat tone of the reaction

$$[AxH_2O, \infty H_2O] = q_\infty - q_x$$

is called the *heat of dilution* of the solution AxH_2O. There is another heat of dilution, however, of importance in the thermodynamical calculations, namely dq/dx, the heat change when one gram-molecule of water is mixed with an indefinitely large quantity of the solution AxH_2O. From what has been already stated, the value of this heat of dilution approaches zero as x increases.

It is sometimes more convenient to express the heat changes when a variable amount of the solute dissolves in one gram-molecule of water, thus

$$[H_2O, yA] = q',$$

where y varies from 0 to the value b corresponding to a saturated solution. When this method of expressing results is employed, the thermodynamically important heat of solution is that given by dq'/dy—

$$\frac{dq'}{dy} = [H_2OyA, dyA] \div dy,$$

and the value of this when saturation is reached is denoted by $(dq'/dy)_b$ and called the *limiting heat of solution.* It expresses the heat change that attends the introduction of a gram-molecule of solute into an indefinitely large amount of solution when a saturated solution is thereby formed.[1]

Some Thermochemical Results.—Very few important theoretical conclusions have been deduced from thermochemistry, despite the enormous amount of experimental data that has been accumulated. One or two important results may be noticed.

As early as 1840 Hess (p. 162) observed that when dilute aqueous solutions of salts are mixed, there is practically no thermal change, provided that no precipitation or gaseous evolution occurs. This is called the Law of Thermo-neutrality of salt solutions. For a number of salts, *e.g.* the halogen salts of cadmium and mercury, it does not hold. A simple explanation of the law is given later (p. 220).

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[1] For tables of heats of solution, the works already cited must be consulted.

The heats of solution of acids and bases in dilute aqueous solution are of great interest. The following table contains a number of the experimental results:—

Reaction.	Heat of Neutralisation.	Reaction.	Heat of Neutralisation.
$HCl + NaOH$ . . .	13·7 Cals.	$HCl + LiOH$ . . .	13·7 Cals.
$HBr + NaOH$ . . .	13·7 ,,	$HCl + KOH$ . . .	13·7 ,,
$HNO_3 + NaOH$ . . .	13·7 ,,	$HCl + \frac{1}{2}Ba(OH)_2$ . .	13·8 ,,
$HIO_3 + NaOH$ . . .	13·8 ,,	$HCl + \frac{1}{2}Ca(OH)_2$ . .	13·9 ,,

The substances mentioned in this table belong to what are called the strong acids and bases (see Chap. VI.), and from the results given, it is clear that, in dilute solution, the neutralisation of one gram-equivalent of a strong acid by a strong base always produces the same thermal change. This regularity no longer holds when either the acids or the bases are weak, as the accompanying figures serve to show:—

Reaction.	Heat of Neutralisation.	Reaction.	Heat of Neutralisation.
$HCl + NH_4.OH$.	12·2 Cals.	$\frac{1}{2}H_2CO_3 + NH_4.OH$ . .	8·4 Cals.
$HCl + NH_2.OH$ . .	9·2 ,,	$\frac{1}{2}H_2S + \frac{1}{2}Ba(OH)_2$ . .	7·8 ,,
$HF + KOH$ . . .	16·3 ,,	$H_2S + NH_4OH$ . .	6·2 ,,
$\frac{1}{2}H_2CO_3 + NaOH$ . .	10·1 ,,	$HCN + NaOH$ . . .	2·8 ,,

Considerable differences are here noticed between the various values. The theoretical bearing of these results is given in Chap. VI.

Thermochemical measurements have been used in studying the basicity of acids and also their relative strengths. These applications also are mentioned in the same chapter.

CHEMICAL AFFINITY.

The property of bodies in consequence of which they undergo chemical change when brought into contact with one another is called *chemical affinity.* Since the operation of chemical affinity is attended with the production of energy, chemical affinity may be regarded as a force. Little is known of the nature of chemical affinity, and at present it is not possible to give an account of chemical change in terms of the operation of definite physical forces. There are, however, good reasons for supposing that the chemical forces which hold together the atoms in a molecule have only a very short range of effective action, their intensity diminishing very rapidly as the distance between the atoms increases.

Although the nature of chemical affinity is still obscure, considerable progress has been made in the study of its mode of operation. The laws which describe the influence of temperature, pressure, concentration, etc., upon chemical change are fairly well understood, and are dealt with later in the present chapter.

The views on affinity held during the eighteenth century may be indicated by reference to the tables of affinity, constructed originally by Geoffroy (1718) and extended considerably by Bergmann.[1] For each substance a table of affinity was constructed, in which other substances were arranged in order of decreasing affinity for the particular substance in question. The interpretation of chemical change adopted in the construction of these tables was this: if a substance A reacts upon a substance BC with the result that AB and C are produced, then the affinity of B for A is greater than the affinity of B for C.

Bergmann gave two tables of affinity for each substance, one "in the dry way" and the other "in the wet way," since he recognised that the results obtained in these two ways were sometimes different; and Stahl (1720) recognised cases in which the relative order of affinities was altered by temperature. Apart from this, however, it was supposed that the chemical affinity of a change depends simply upon the nature of the substances concerned, and that a change proceeds to completion in the direction of the stronger affinity, *e.g.* in the case already mentioned, the stronger affinity of B for A overcomes the weaker affinity of B for C.

The insufficiency of this view was recognised by Berthollet,[2] who showed that many chemical changes which at that time were supposed to proceed exclusively in one direction could be reversed, *e.g.* that although baryta and potassium sulphate react to produce barium sulphate and potash, it is possible to cause the two last-named substances to react with the formation of the substances first mentioned. Berthollet clearly pointed out that the direction in which a change proceeds depends not only upon the nature of the substances concerned, but also upon their relative "quantities," and regarded a chemical change that proceeds to completion as being an exceptional and not a normal case. He did not succeed, however, in arriving at the correct estimate of chemical "quantity," and since he also disputed the validity of the law of fixed ratios (*vide* Chap. I.), his views met with little support. Later the "influence of mass" was recognised by Rose,[3] Malaguti,[4] Wilhelmy,[5] Gladstone,[6] Berthelot and Péan de St Gilles,[7] and others, but it was due largely to the work of Guldberg and Waage[8] that this influence received mathematical expression, in their formulation of the *Law of Mass Action*. In the subsequent development of the subject the application of the laws of thermodynamics has proved of the utmost value.[9]

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[1] Bergmann, *De Attractionibus Electivis* (Upsala, 1775); English translation, 1785.

[2] Berthollet, *Essai de Statique Chimique* (Paris, 1801-2); English translation, 1804.

[3] Rose, *Pogg. Annalen*, 1842, **55**, 415; 1851, **82**, 545; 1855, **94**, 481; 1855, **95**, 96, 284, 426.

[4] Malaguti, *Ann. Chim. Phys.*, 1857, (iii.), **51**, 328.

[5] Wilhelmy, *Pogg. Annalen*, 1850, **81**, 413, 499.

[6] Gladstone, *Phil. Trans.*, 1855, **145**, 179; *Trans. Chem. Soc.*, 1856, **9**, 54.

[7] Berthelot and Péan de St Gilles, *Ann. Chim. Phys.*, 1862, (iii.), **65**, 385; **66**, 5; 1863, **68**, 225.

[8] Guldberg and Waage, *Études sur les affinités chimiques* (Christiania, 1867); *J. prakt. Chem.*, 1879, (ii.), **19**, 69; Ostwald's *Klassiker*, No. 104.

[9] For an account of the historical development of this part of the subject, the reader is referred to the works cited on p. 169.

The study of thermochemistry is associated with what was, in effect, a revival of the old view of affinity as propounded by Bergmann. In 1854 J. Thomsen[1] put forward the principle that "every simple or complex effect of a purely chemical nature is accompanied by production of heat." Later, a similar "law" was enunciated by Berthelot[2] under the name of the "*law of maximum work*." It may be stated in the form that "every chemical change accomplished without the addition of external energy tends to the formation of that body or system the production of which is accompanied by the development of the maximum quantity of heat." This so-called law cannot be accepted as a law of Nature, but only as an approximate rule, for although it is true that at ordinary temperatures the majority of chemical changes that take place are exothermic, yet at high temperatures endothermic bodies can be formed by the direct union of their elements, and further, it is impossible by this law to account for the occurrence of reversible reactions.

In fact, the condition[3] that a physical or chemical change may take place in an isolated system is not that an evolution of heat shall occur, but that the *entropy* of the system shall be thereby increased. When an isothermal change is considered, and not change in an isolated system, the necessary condition for change to proceed is that the thermodynamic potential at constant volume shall be diminished by the process. This function, which is also known as the *free energy* of the system, is such that, in an isotherma change, the change in the free energy of the system measures the maximum amount of work that can be gained by the change (*i.e.* the work gained when the reaction proceeds isothermally in a thermodynamically reversible manner). The change in free energy may therefore be looked upon as a measure of the work accomplished by the chemical affinity operative in producing the change. For the measurement of chemical affinity in terms o free energy, however, the reader must be referred to works on physica chemistry.[4]

CHEMICAL EQUILIBRIUM.[5]

Reversible Reactions. — When calcium carbonate is heated to a (constant) high temperature it decomposes into calcium oxide and carbon dioxide, and if the experiment is effected in an open vessel the carbon dioxide diffuses away into the air and after a sufficient length of time the decomposition is complete. The case is different when the decomposition is carried out in a closed vessel so that the volatile product of the change cannot escape Under these conditions chemical change proceeds as usual, but eventually it ceases, and in general[6] the cessation of chemical change sets in while there is still present unchanged calcium carbonate. The quantities of calcium carbonate, carbon dioxide, and calcium oxide present in the system then remain unchanged and independent of the time, and a state of *equilibrium* is said to have been reached.

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[1] Thomsen, *Pogg. Annalen*, 1854, 92, 34.

[2] Berthelot, *opus. cit.* (p. 162); *Compt. rend.*, 1867, 64, 413; 1870, 71, 303; *Ann Chim. Phys.*, 1869, (iv.), 18, 103.

[3] Derived from thermodynamic considerations.

[4] *E.g.* Nernst, *Theoretical Chemistry*, translated by Tizard, 3rd English edition (Macmillan & Co., 1911); *Applications of Thermodynamics to Chemistry* (Scribner & Sons, New York, 1907); also Planck, *Thermodynamics*, translated by Ogg (Longmans & Co., 1903).

[5] For a full account of the subjects discussed in the remainder of this chapter the reader is referred to the following works: Nernst, *Theoretical Chemistry*, translated by Tizard, 3rd edition, 1911; Van't Hoff, *Lectures on Theoretical and Physical Chemistry*, translated by Lehfeldt (Arnold, 1899); Van't Hoff and Cohen, *Studies in Chemical Dynamics*, translated by Ewan (Williams & Norgate, 1896); Mellor, *Chemical Statics and Dynamics* (Longmans & Co., 1904); and the works cited on p. 177.

[6] Provided the quantity of carbonate taken does not fall below a certain minimum.

This result is explained when it is recalled that calcium oxide and carbon dioxide can unite to form calcium carbonate, and accordingly do so as soon as they are produced by the decomposition of calcium carbonate. Thus two changes go on, one of which at first partly, and eventually wholly, undoes the work of the other, and a state of balance is at length reached.

Chemical changes like the preceding are called *balanced* or *reversible* reactions. Many decompositions are reversible, as has been already mentioned, and reversible decomposition is known as dissociation (p. 160). Reversible changes are frequently encountered, however, in other types of chemical reactions. For instance, the change

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

is reversible. The continued addition of water to bismuth trichloride leads to the precipitation of more and more bismuth oxychloride until eventually the bismuth is practically all precipitated. On the other hand, the addition of more and more hydrochloric acid to bismuth oxychloride leads to the reverse change, the whole of the oxychloride eventually passing into solution. The reaction

$$2SbCl_3 + 3H_2S \rightleftharpoons Sb_2S_3 + 6HCl$$

furnishes another example. The passage of hydrogen sulphide into a solution of antimony trichloride in dilute hydrochloric acid leads to precipitation of antimony trisulphide; but the last-named substance passes into solution when warmed with concentrated hydrochloric acid, and hydrogen sulphide is evolved. There are, however, many reactions which apparently are not reversible, *e.g.* the union of aluminium and oxygen, the decomposition of ammonium nitrite into water and nitrogen, etc.

The solution of metals in acids was at one time regarded as a type of irreversible reactions, but Ipatieff and Werchowsky[1] showed in 1909 that by subjecting the aqueous solutions of certain metallic salts to high pressures of hydrogen gas at slightly raised temperatures, the metals could be precipitated out of solution. Hence the apparent irreversible nature of such reactions as

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

under ordinary conditions is attributable to the fact that one of the products, namely hydrogen, is removed from the sphere of action.

Chemical equilibrium, like physical equilibrium, must be looked upon as *dynamic*, and not as static equilibrium. The equilibrium between liquid and vapour at constant temperature, for instance, is looked upon as being the result of two changes which are proceeding at equal rates—viz. the evaporation of liquid and the condensation of vapour, the one undoing the work of the other. In the same way, two reactions are still to be regarded as proceeding when a chemical equilibrium is observed and all change has apparently ceased, only the reactions proceed at equal rates and are mutually antagonistic. During the period preceding the establishment of equilibrium, then, the observed change must be attributed to the fact that the speed of the initial (forward) change is greater than that of the reverse change. As time goes on, however, the speed of the forward change diminishes, or that of the reverse change increases, or both of these occur, and eventually the forward and backward changes proceed at equal rates. Since increase and decrease of speed on this view are associated with increase and decrease of concentration of the starting materials[1] respectively, some connection may naturally be supposed to exist between the rate at which a chemical change is proceeding at any moment and the concentration of the reacting materials at that moment. This conclusion is borne out by experiment, as will be seen later.

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[1] Ipatieff and Werchowsky *Ber.*, 1909, **42**, 2078.

The idea that chemical equilibrium is dynamic was originally proposed by Williamson[2] in his classic researches on etherification, but its acceptance as an adequate interpretation of the nature of chemical equilibrium in general only came after the work of Clausius, Maxwell and others had led to the development of the Kinetic Theory, and thereby enabled a mental picture to be drawn of the nature of chemical change. The application of the Kinetic Theory to the interpretation of the nature of chemical change was first made by Pfaundler[3] in 1867.

Homogeneous Systems; The Law of Chemical Equilibrium.—The homogeneous *gaseous* systems will be dealt with first. Suppose that n_1, n_2, n_3 . . . molecules of the gaseous substances of molecular formulæ A, B, C . . . respectively react to produce m_1, m_2, m_3 . . . molecules of the gaseous products of the formulæ P, Q, R . . .

$$n_1A + n_2B + n_3C + \ldots \longrightarrow m_1P + m_2Q + m_3R + \ldots$$

Then, at constant temperature, the relationship between the concentrations of the various substances concerned in the equilibrium may be expressed in the following manner:—

$$\frac{[P]^{m_1} \times [Q]^{m_2} \times [R]^{m_3} \times \ldots}{[A]^{n_1} \times [B]^{n_2} \times [C]^{n_3} \times \ldots} = K,$$

where a formula enclosed in square brackets indicates the concentration[4] of the substance of that formula when equilibrium is reached, and **K** is a constant, known as the *equilibrium constant*. This equation constitutes the *law of chemical equilibrium*. It can be deduced thermodynamically for a system comprised of perfect gases, and may also be arrived at from considerations based upon the kinetic theory.

The meaning of the law may be explained by reference to one or two examples. At temperatures above 180°, hydrogen iodide is observed to decompose into hydrogen and iodine. Since at these temperatures, hydrogen and iodine unite to form hydrogen iodide, the change is a reversible one—

$$2HI \rightleftharpoons H_2 + I_2.$$

---

[1] The starting materials for the reverse change are the final products of the forward change, and the speed of a chemical reaction is measured by the rate at which the starting materials disappear.

[2] Williamson, *Annalen*, 1851, 77, 37; *Alembic Club Reprints*, No. 16.

[3] Pfaundler, *Pogg. Annalen*, 1867, 131, 57.

[4] Concentrations are usually expressed in gram-molecules per c.c. or per litre. The concentrations are obviously proportional to the respective partial pressures of the substances.

If, then, hydrogen iodide is maintained at a constant temperature above 180°, say at the boiling-point of sulphur (445°), in a closed vessel until equilibrium is established, the following relationship holds good:—

$$[H_2] \times [I_2]/[HI]^2 = K.$$

An interesting result at once follows. If a, b, c denote the number of gram-molecules of hydrogen, iodine and hydrogen iodide in the system at equilibrium, and V denotes the total volume,

$$[H_2] = a/V, \quad [I_2] = b/V, \quad [HI] = c/V,$$

and the preceding equation becomes

$$ab/c^2 = K.$$

Expressing the result in words, the state of equilibrium is independent of the volume (and therefore the pressure) of the system. That such is the case has been shown experimentally by Bodenstein.[1]

At the boiling-point of sulphur, Bodenstein found that equilibrium was reached when 22 per cent. of hydrogen iodide was decomposed; hence $a : b : c :: 11 : 11 : 78$, and $K = 0{\cdot}01984$. It is now possible to deduce beforehand the state of equilibrium attained when hydrogen and iodine are brought together in any ratio at the boiling-point of sulphur. If for each gram-molecule of hydrogen taken, d gram-molecules of iodine are taken, and $2e$ gram-molecules of hydrogen iodide are produced before equilibrium is reached, the amounts of hydrogen and iodine left uncombined are $(1-e)$ and $(d-e)$ gram-molecules respectively, and

$$(1-e)(d-e)/(2e)^2 = 0{\cdot}01984.$$

Hence, from the known value of d, the value of $2e$ may be calculated. The results calculated in this manner agree very well with those obtained experimentally, as the following numbers serve to show (Bodenstein, *loc. cit.*):—

Hydrogen Taken.	Iodine. Taken.	Hydrogen Iodide	
		Found.	Calculated.
8·10	2·94	5·64	5·66
7·94	5·30	9·49	9·52
8·07	9·27	13·47	13·34
8·12	14·44	14·93	14·82
8·02	27·53	15·54	15·40
7·89	33·10	15·40	15·12

For each experiment cited in the table, the numbers given under hydrogen, iodine, and hydrogen iodide are proportional to the initial concentrations of the first two substances and the equilibrium concentration of the third (its initial concentration being zero).

For the dissociation of nitrogen peroxide—

$$N_2O_4 \rightleftharpoons 2NO_2,$$

---

[1] Bodenstein, *Zeitsch. physikal. Chem.*, 1897, **22**, 1.

the condition of equilibrium at constant temperature is

$$[NO_2]^2/[N_2O_4] = K.$$

If, then, a and b denote the number of gram-molecules of NO_2 and N_2O_4 respectively when the system is in equilibrium, and V denotes the volume, the equation becomes

$$a^2/bV = K.$$

Hence, in this case, the state of equilibrium varies with the volume.[1] Clearly, if the volume is increased, then a must increase and b diminish in order that the expression a^2/bV shall remain constant; in other words, the degree of dissociation of nitrogen peroxide is increased by increase of volume. The degree of dissociation may be readily calculated from the observed density of the system, and the results obtained are in satisfactory accordance with the requirements of the law of chemical equilibrium (*vide supra*, p. 142).

The dissociation of phosphorus pentachloride

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

may be similarly treated. The condition of equilibrium is that

$$[PCl_3] \times [Cl_2]/[PCl_5] = K.$$

Suppose, now, that into the system (in equilibrium) an excess of chlorine is introduced and the system brought to its original volume. The result is easy to foretell. Since $[Cl_2]$ has been increased, it is clear that the only way in which the expression on the left-hand side of the latter equation can maintain its former value is for $[PCl_3]$ to diminish and $[PCl_5]$ to increase.[2] The general result which this illustrates may be expressed in words as follows:—*The degree of dissociation of a substance is diminished by increasing the concentration of one of the products of dissociation.*

Passing from gaseous systems to the consideration of equilibrium in liquid solutions, it may be stated that the same law of chemical equilibrium holds good for these equilibria as holds for gaseous equilibria, provided that the osmotic pressure of each of the substances participating in the equilibria follows the laws of Boyle and Gay-Lussac. The thermodynamic proof was given by Van't Hoff,[3] and the restrictions under which the proof holds good limit the exact application of the law of chemical equilibrium to dilute solutions.[4]

As an example, the dissociation of nitrogen peroxide may be referred to again. This change occurs not only in the gaseous state, but also when the peroxide is dissolved in a solvent upon which it has no chemical action. From measurements of the degree of dissociation of the peroxide in chloroform solutions of varying concentration,[5] it has been shown[6] that the law of chemical equilibrium satisfactorily expresses the results.

Heterogeneous Systems; Extension of Law of Chemical Equilibrium.—It is possible to extend the law of chemical equilibrium to the liquid and gaseous phases of heterogeneous systems. For example, consider the reaction

---

[1] This is the case whenever the change leads to an alteration in the total number of molecules present.

[2] Increase in one of these concentrations necessitates a decrease in the other, from chemical considerations.

[3] Van't Hoff, *K. Svenska Vet.-Akad. Handl.*, 1885, 21, 38; *Zeitsch. physikal. Chem.*, 1887, 1, 481; *Phil. Mag.*, 1888, [v.], 26, 81.

[4] *Cf.* Chap. VI.

Cundall, *Trans. Chem. Soc.*, 1891, 59, 1076.

[6] Ostwald, *ibid.*, 1892, 81, 242.

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

taking place at constant temperature in a closed vessel. The system consists of two solid phases and a gaseous phase. Now every solid may be regarded as possessing a vapour pressure (sublimation pressure, *vide* p. 46), although it may be too small to admit of experimental determination, and at constant temperature the vapour will be in equilibrium with the solid at a definite pressure, which cannot vary so long as solid phase is present. Accordingly, in the equilibrium equation for the gaseous phase—

$$\frac{[CaO].[CO_2]}{[CaCO_3]} = K,$$

the concentrations [CaO] and [CaCO$_3$], which represent concentrations of saturated vapours at constant temperature, are constant quantities. The equation therefore reduces to

$$[CO_2] = \text{constant}.$$

In other words, to each temperature there corresponds a definite partial pressure (or concentration) of carbon dioxide at which the gas is in equilibrium with the two solid phases. This pressure is practically identical with the total pressure of the gaseous phase, and is called the *dissociation pressure*.

From the preceding discussion it is easy to see that the following general rule may be stated for arriving at the condition of equilibrium in a heterogeneous system of solid and gaseous phases at constant temperature. Write down the left-hand side of the equilibrium equation given on p. 171, omitting all factors that refer to substances present as solid phases; the expression so obtained has a constant value. For instance, the dissociation of solid ammonium hydrosulphide

$$NH_4HS \rightleftharpoons NH_3 + H_2S$$

leads to the condition of equilibrium

$$[NH_3].[H_2S] = \text{constant},$$

which has been shown experimentally to be the case.[1]

Equilibrium in other heterogeneous systems can be discussed in a manner similar to the above.[2]

Heterogeneous Systems: the Phase Rule.—The conditions of equilibrium in a heterogeneous system may be expressed in a manner quite independent of the atomic and molecular theories by means of the *Phase Rule*. This rule, which applies to both chemical and physical equilibria, was deduced thermodynamically by Willard Gibbs in 1874,[3] but its practical applications were first made by Roozeboom.

The equilibrium in a system is described by the Phase Rule in terms of the number of phases, components, and degrees of freedom of the system.

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[1] Isambert, *Compt. rend.*, 1881, 92, 919; 1881, 93, 731; 1882, 94, 958.

[2] See Nernst, *Theoretical Chemistry*, translated by Tizard, (Macmillan & Co., 3rd edition, 1911), Book III., chap. iii.

[3] Willard Gibbs, *Trans. Connecticut Acad.*, 1875-8, 2 and 3.

The meaning of the term *phase* has already been given (p. 6) and is easy to understand. It is rather more difficult to understand the meaning of the term "component," since by the components are not understood the constituents of a system. It may be said at once that the components of a system may be chosen in more than one way, but it is only their *number* that is of importance. The *number of components* of a system is the least number of constituents, the quantities of which are independently variable, in terms of which the composition of each phase may be expressed.[1] For example, consider a saturated solution of sodium sulphate in equilibrium with vapour and the solid decahydrate $Na_2SO_4.10H_2O$. The number of components is two. The anhydrous salt Na_2SO_4 and water may be chosen, since the amounts of these substances in the system are independently variable. In terms of these substances the composition of each phase may be expressed. The solid phase is $Na_2SO_4 + 10H_2O$, the liquid phase $Na_2SO_4 + xH_2O$, and the gaseous phase, $0Na_2SO_4 + H_2O$ (zero and negative amounts are permissible when expressing the composition of a phase in terms of the components).

The Phase Rule applies to systems in which equilibrium is dependent only upon the variables (i.) temperature, (ii.) pressure, and (iii.) composition of the phases. The least number of these variables which must be arbitrarily fixed in order that the condition of a system may be perfectly defined, is called the number of *degrees of freedom* of the system. For instance, take the system water in contact with its vapour. If the temperature is arbitrarily chosen to have a certain value, the system is perfectly defined. Equilibrium is then possible only at a certain pressure, determined by the system itself, either evaporation of water or condensation of vapour occurring until this pressure, the vapour pressure of water at the particular temperature chosen, is reached. Hence the system has one degree of freedom. Systems with 0, 1, 2 . . . etc., degrees of freedom are said to be *invariant*, *univariant*, *bivariant*, . . . etc.[2]

The *Phase Rule* states the condition of equilibrium in a heterogeneous system as follows:—

$$P + F = C + 2,$$

where P = number of phases, F = number of degrees of freedom, and C = number of components of the system.

The application to systems of one component may be briefly outlined. Here each phase has the same chemical composition, and hence change of composition does not enter into the discussion. Two phases in equilibrium constitute a univariant system, and hence if either the temperature or the pressure be arbitrarily maintained at a constant value there will be a corresponding value of the other variable for the system to be in equilibrium. Both values cannot be arbitrarily chosen; one being chosen arbitrarily by the experimenter, the appropriate value of the other is chosen by the system, so to speak. Thus, in the system *liquid – vapour*, corresponding to each temperature chosen there is a definite pressure, characterised by the particular system under investigation, at which equilibrium occurs. This is the vapour pressure of the liquid (see p. 34). For the system *solid – vapour* in equilibrium, there is likewise a definite equilibrium pressure corresponding to each temperature, viz. the sublimation pressure (see p. 46). In the case of the system *solid – liquid*, the interpretation is that the temperature of equilibrium, or melting-point of the solid, varies with the pressure (see p. 43). It is further possible for systems *solid – solid* to occur, *e.g.* rhombic sulphur-monoclinic sulphur, which are in equilibrium at the transition-point (see p. 69). The system, being univariant, the transition-point must vary with the pressure.

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[1] See Trevor, *J. Physical Chem.*, 1896, I, 22.

[2] Trevor, *ibid*, 1902, 6, 136.

When three phases are present in equilibrium, the system is invariant. Accordingly the equilibrium is only observed when the temperature and pressure possess certain fixed values, defined by the system itself. That is to say, the values may be experimentally determined, but neither of them can be arbitrarily selected. Such a system is said to be at the *triple* point, and the equilibrium temperature and pressure are referred to as the triple point temperature and pressure respectively. The three phases *solid-liquid-vapour* are in equilibrium at the triple point in the case of a substance that forms only one solid phase and one liquid phase. On a pressure-temperature diagram the conditions of equilibrium in univariant systems are represented by curves, as, for example, the sublimation curve and the vapour pressure curve. The triple point in the system *solid – liquid-vapour* is represented by the point of intersection of these two curves (see p. 47).

Other invariant systems are possible, such as *solid phase A – solid phase B – vapour*, when the substance is polymorphic, and with substances which exist in two liquid phases (liquid crystals), invariant systems such as *liquid phase A – liquid phase B – vapour* are possible.[1]

The systems of which sodium sulphate and water are the components furnish simple examples of two component systems. Since a single phase in a two-component system has three degrees of freedom, the composition of a solution of sodium sulphate does not possess a definite value even when both temperature and pressure are fixed, but may be varied at will between certain limits. When, however, another phase is also present, say the decahydrate $Na_2SO_4.10H_2O$, the system has only two degrees of freedom, and having fixed the value of the pressure, the state of the system *solution – decahydrate* is fixed as soon as either the temperature or the composition of the solution is specified. When the temperature is given, there is only one composition of solution for the system to be in equilibrium, and, conversely, if the composition of the solution be defined, there is only one temperature at which this solution can exist in equilibrium with the decahydrate. Such a solution is said to be saturated at the particular temperature and pressure in question, and it is therefore seen from this example that the term "saturated solution" only acquires a definite meaning when the nature of the solid phase in contact with the solution is specified. As has been previously remarked (p. 110), at a definite pressure and temperature and in the absence of the solid phase, a solution may contain more sodium sulphate that the solution in equilibrium with the solid phase, the solution being termed "supersaturated." Yet a solution supersaturated with respect to the decahydrate may still be unsaturated with respect to the heptahydrate $Na_2SO_4.7H_2O$.

When sodium sulphate decahydrate is heated to 32·4° it decomposes into anhydrous salt and water—

$$Na_2SO_4.10H_2O \rightleftharpoons Na_2SO_4 + 10H_2O,$$

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[1] For the latter, see Hulett, *Zeitsch. physikal. Chem.*, 1899, **28**, 629.

and during the change the temperature remains constant. This is what would be expected from the Phase Rule. The system *decahydrate – anhydrous salt – saturated solution* is only univariant, and hence at a definite pressure arbitrarily chosen (atmospheric as a rule) equilibrium occurs only at one particular temperature and with the solution at one particular concentration. This *transition-point*, however, varies with the pressure. The system *decahydrate – anhydrous salt – solution-vapour* is invariant, and can only exist therefore at fixed values of temperature and pressure, defined by the system itself, and not capable of being arbitrarily selected.

The fact that the solubility curve of sodium sulphate consists of two parts, intersecting at a sharp angle, is easy to understand from the preceding discussion. The two parts of the curve represent conditions of equilibrium in the two systems *decahydrate – solution* and *anhydrous salt – solution* respectively, at atmospheric pressure, and intersect at a point which gives the equilibrium temperature and composition for the system *decahydrate – anhydrous salt – solution* at atmospheric pressure.

In the light of the Phase Rule, the dissociation of calcium carbonate is easily discussed. The dissociating system is one of two components and three phases (two solid, one gaseous), and hence is univariant. At any temperature arbitrarily chosen, therefore, equilibrium obtains at one particular pressure only. The result thus deduced agrees with that previously arrived at in another way (p. 174).

Considerations of space prevent a more detailed account of applications of the Phase Rule from being given, and reference must therefore be made to the text-books[1] for further information. Owing to the rather abstract nature of the subject, however, an example may be given to illustrate the manner in which the Phase Rule proves of service to the chemist.

It was discovered by Weyl[2] that sodium and potassium dissolve in liquid ammonia, forming very remarkable solutions. When dilute they are blue; the concentrated solutions exhibit metallic reflection and appear bronze-coloured and opaque. In studying these solutions, Joannis[3] considered that he had isolated the solid compounds $NaNH_3$ and KNH_3 from them. Briefly, he observed that, at constant temperature, the pressure in the system *solution – vapour* fell as ammonia was withdrawn, until a solid was precipitated. This solid appeared bronze-coloured by reflection. Thereafter, although ammonia was continuously withdrawn from the system, the equilibrium pressure remained constant, until only the system *free metal – ammonia gas* was left. The free metal appears white by reflection. Joannis explained the results as follows. The pressure remains constant at the vapour pressure of the saturated solution from the moment that the compound is precipitated until the continued withdrawal of ammonia causes the phase *solution* to disappear. The compound then dissociates into metal and ammonia at a constant dissociation pressure, which is *equal to the vapour pressure of the saturated solution*, and hence only one equilibrium pressure is observed in the experiment.

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[1] Bancroft, *The Phase Rule* (Cornell University, New York, 1895); Roozeboom, *Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre* (Brunswick, 1901); Findlay, *The Phase Rule and its Applications* (Longmans & Co., 3rd edition, 1911).

[2] Weyl, *Pogg. Annalen*, 1864, **121**, 601.

[3] Joannis, *Compt. rend.*, 1889, **109**, 900.

Roozeboom[1] pointed out that the assumption made by Joannis with regard to pressures was unnecessary, since an explanation was supplied by the Phase Rule. The system *compound* - *metal* - *solution* - *vapour* would be invariant (2 components, 4 phases), and only exists at a single temperature and pressure. At this invariant-point temperature, the univariant systems *compound* - *solution* - *vapour* and *compound* - *metal* - *vapour* would have the same equilibrium pressures. Hence Roozeboom suggested that Joannis had carried out his experiments in each case at the invariant point temperature. Joannis showed, however, that the phenomena he described were noticed *at a series of different temperatures.* This proves conclusively that no solid compounds are precipitated, only one solid phase ever being present, and that being, as was clearly seen towards the end of an experiment, the metal itself. In short, the divariant system *solution* - *vapour* exhibits, at constant temperature, a variation of vapour pressure with variation of composition of solution. With the precipitation of metal, a univariant system *metal* - *solution* - *vapour* is obtained, and accordingly at constant temperature the system exhibits a constant vapour pressure during the withdrawal of ammonia until the phase *solution* disappears and the divariant system *metal* - *gas* is left behind[2] The "bronze-coloured compounds" are merely free metal covered with a layer of saturated solution, the surface tension between solution and metal being extraordinarily great. It has, in fact, been clearly shown that when the system contains considerably less than one gram-molecule of ammonia to one gram atom of sodium the liquid phase is still present.[3]

Displacement of Equilibrium.—When a system is in equilibrium, and one of the factors of equilibrium (temperature, pressure, etc.) is altered, the state of equilibrium is disturbed and change occurs in the system. For instance, in the case of the system $CaCO_3 - CaO - CO_2$, which at a definite temperature is in equilibrium at one particular pressure, if the temperature or the pressure be altered, then, according to circumstances, either more carbonate dissociates or else combination of its products of dissociation proceeds to some extent; and in this instance, if either of the factors of equilibrium is made to assume permanently a new value while the other is kept fixed at the original equilibrium value, the change within the system continues until one of the phases disappears. A new state of equilibrium can, however, be established if the second factor of equilibrium be likewise allowed to change. In the case of an invariant system it is, of course, impossible to alter permanently any one of the factors of equilibrium without causing the disappearance of at least one phase, since there is but one set of conditions under which equilibrium is possible.

The *direction* in which change proceeds when a system in equilibrium has one of the factors of equilibrium altered may be predicted by the application of *Le Chatelier's Theorem.*[4] This is stated by Ostwald in the following form:—*If a system in equilibrium is subjected to a constraint by which the equilibrium is shifted, a reaction takes place which opposes the constraint,* i.e. *one by which its effect is partially destroyed.* Bancroft's statement is that *any change in the factors of equilibrium from outside is followed by a reverse change within*

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[1] Roozeboom, *Compt. rend.*, 1890, **110**, 134.

[2] Ruff and Geisel, *Ber.*, 1906, **39**, 828; Kraus, *J. Amer Chem. Soc.*, 1908, **30**, 653.

[3] For the necessary modification of the Phase Rule when applied to divided systems, *e.g.* colloids, see Tolman, *J. Amer. Chem. Soc.*, 1913, **35**, 307, 317; *cf.* Pavlow, *Zeitsch. physikal. Chem.*, 1910, **75**, 48.

[4] Le Chatelier, *Compt. rend.*, 1884, **99**, 786; Braun, *Wied. Annalen*, 1888, **33**, 337.

the system. To continue with the illustration already chosen, suppose that heat is supplied to the system and its temperature thereby raised. The change that occurs must either be the dissociation or the re-formation of calcium carbonate, and according to the theorem quoted that change occurs which absorbs heat, viz. the dissociation of the carbonate. On the other hand, if at constant temperature the pressure upon the system is increased, change proceeds, according to the theorem, in the direction which diminishes pressure, *i.e.* in the direction associated with contraction in volume. Accordingly, the quantity of carbonate increases at the expense of the quicklime and carbon dioxide until the pressure of the latter falls to that of the dissociation pressure.

Again, consider the system *solid – liquid* in equilibrium at a definite temperature and pressure. An increase of pressure favours transformation into the phase possessing the smaller specific volume. Hence either liquid freezes or solid melts according as the solid expands or contracts on melting. The first is the more usual case, and the process of freezing being associated with an evolution of heat, equilibrium will be re-established at a higher temperature than before, *i.e.* the melting-point is raised by increase of pressure. The second case is typified by ice, bismuth, gallium, a number of other substances, and the melting-point is lowered by increase of pressure.

In a similar manner the theorem may be employed to deduce that, at constant temperature, the solubility of a salt in a liquid is increased or diminished by increase of pressure according as the process of solution is attended by contraction or expansion; and that, at constant pressure, the solubility is increased or decreased by rise of temperature according as the limiting heat of solution (*vide* p. 166) is negative or positive, *i.e.* represents absorption or evolution of heat respectively.

Applied to chemical systems, the general result is obtained that (i.) at constant pressure, rise of temperature favours the change that occurs with absorption of heat, and that (ii.) at constant temperature, increase of pressure promotes the change that is associated with diminution in volume. Thus, considering the change

$$N_2O_4 \rightleftharpoons 2NO_2$$

which occurs in the direction $\rightarrow$ with heat absorption, it follows that the degree of dissociation of nitrogen peroxide is increased by a rise of temperature and diminished by an increase of pressure.

It is easy to see, from the fact that endothermic reactions are promoted by rise of temperature, why such endothermic compounds as carbon disulphide, nitric oxide, acetylene, etc., should be produced at high temperatures by the direct union of their elements, although at ordinary temperatures these substances are unstable. The production of ozone from oxygen at extremely high temperatures[1] is also accounted for, the reaction being strongly endothermic.

In order to predict *quantitatively* the extent of displacement of equilibrium, it is necessary to have recourse to the second law of thermodynamics. The most useful deduction from this law for the present purpose is the theorem, which may be stated verbally in the following way[2]:—*The latent heat of expansion of a system is equal to the product of the absolute temperature and the*

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[1] Fischer and Braehmar, *Ber.*, 1906, 39 940.

[2] The theorem is expressed mathematically later on.

increment of pressure per degree of temperature at constant volume.[1] The application of this theorem to systems composed of perfect gases enables the connection between displacement of equilibrium and change of temperature to be mathematically formulated. The relationship is as follows:—

$$\frac{d}{dT}(\log_e K) = -\frac{Q}{2T^2},$$

where K is the equilibrium constant (defined by the equation on p. 171) for the system at the absolute temperature T, and Q, measured in gram-calories, is the heat of reaction at constant volume for the forward change (*i.e.* the change from left to right in the equation on p. 171). This differential equation was deduced by Van't Hoff.[2] Its application may be extended to dilute solutions, and, by deriving the value of K in accordance with the rule previously stated (p. 174), to the fluid phases of heterogeneous systems also.

On the assumption that Q does not vary with the temperature, the equation may be readily integrated, giving

$$\log_e \frac{K_2}{K_1} = \frac{Q}{2}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

where K_1 and K_2 are the values of K at the temperatures T_1 and T_2 respectively. The assumption requires that the two temperatures shall be fairly close together. Hence it becomes possible to calculate heats of reaction from measurements of equilibrium constants, and conversely, from thermochemical data to deduce the influence of temperature upon chemical equilibrium.

The applications of the preceding equations are dealt with in works on physical chemistry. As a simple illustration, the change

$$NH_4HS \rightleftharpoons NH_3 + H_2S$$

may be considered. If the ammonia and hydrogen sulphide are present in equivalent amounts, the condition of equilibrium (*vide* p. 174) is

$$[NH_3] \cdot [H_2S] = K[NH_3]^2.$$

Denoting the partial pressure of the ammonia by p, the relationship

$$[NH_3] = \frac{p}{RT}$$

follows from the gas laws; and hence

$$\frac{Q}{2}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = 2 \log_e \frac{p_2 T_1}{p_1 T_2}.$$

From this equation and Isambert's data,[3]

when $T_2 = 298{\cdot}1°$, $p_2 = 250{\cdot}5$ mm.,
$T_1 = 282{\cdot}5°$, $p_1 = 87{\cdot}5$ mm.,

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[1] Maxwell, *Theory of Heat*, 10th edition (Longmans & Co., 1891); Lehfeldt, *Physical Chemistry* (Arnold, 1899), p. 146 The theorem is sometimes referred to as Maxwell's third thermodynamic relationship.

[2] Van't Hoff, *K. Svenska Vet.-Akad. Handl.*, 1885, **21**, 38; *Zeitsch. physikal. Chem.*, 1887, **1**, 481.

[3] Isambert, *Compt. rend.*, 1881, **92**, 919.

it is easily calculated that Q is equal to − 21,400 cals. The experimental value for Q, the heat of sublimation of ammonium hydrosulphide at constant volume, is between − 21,640 and − 21,840 cals.[1]

The application of the thermodynamic theorem already quoted (p. 179) to heterogeneous equilibrium is simple, and it is of great use in dealing with the passage of matter from one phase to another. If L denotes the heat (measured in units of energy) absorbed when at the absolute temperature T a definite quantity of matter passes from one phase to another, and at constant temperature the increase in volume associated with the process is *dv*, the theorem becomes

$$\frac{L}{T.dv} = \left(\frac{dp}{dT}\right)_v,$$

where the right-hand side denotes the rate of increase of pressure upon the system with rise of temperature at constant volume.

This equation may be applied to the solution of such problems as the change of melting-points and transition-points with pressure, change of vapour pressure with temperature, change of solubility with temperature and pressure, etc. For example, at a pressure of 1 atmosphere ice melts at 273°. One gram of ice *absorbs* 80 calories, *i.e.* $80 \times 41{\cdot}8 \times 10^6$ ergs on melting, and the *increase* in volume is − 0 0908 c c , *i e.* there is a contraction. Hence,

$$\frac{dp}{dT} = -\frac{80 \times 41{\cdot}8 \times 10^6}{273 \times {\cdot}0908} = -135 \times 10^6 \text{ dynes per sq. cm per degree}$$

$$= -133 \text{ atmospheres per degree.}$$

That is to say, an increase of pressure *lowers* the melting-point of ice, but only by 0·0075° per atmosphere.

From the preceding example it will be seen that the influence of pressure upon the equilibrium is very small. This is a general characteristic of systems from which the vapour phase is absent Such systems are called *condensed systems*, and it will be seen that transition-points, *i.e.* equilibrium temperatures in condensed systems, must be practically identical with invariant point temperatures; for instance, the triple-point temperature for the system *ice – water – vapour* is − 0·0075° C., the transition-point, *i.e.* the melting-point, being 0° C.

RATE OF CHEMICAL CHANGE.

Homogeneous Systems.—In dealing with *velocity of reaction* it is no longer possible to apply directly the principles of thermodynamics to the study of the subject. In seeking experimentally the connection between rate of change and concentration of the reacting substances, however, help is afforded indirectly if it be recollected that the law thus arrived at should be capable. on the dynamic view of chemical equilibrium, of leading to the *law of chemical equilibrium* (p. 171), which has a thermodynamic basis.

For homogeneous systems, such as gaseous systems at not too great pressures, and dilute solutions, the experimental law which describes velocity of reaction is the *Law of Mass Action*, which may be stated thus:—

At constant temperature the rate at which a chemical change is proceeding

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[1] This example is taken from Van't Hoff and Cohen, *Studies in Chemical Dynamics*, translated by Ewan (Williams & Norgate, 1896).

at any moment is proportional to the concentration, at that moment, of each molecule of each substance taking part in the change, i.e. *proportional to the product of these concentrations.*

"Rate of change" or "velocity of reaction" signifies the rate at which the initial substances are disappearing, or, what is the same thing, the rate at which the products of the change are accumulating; and it may be measured by the diminution of concentration of any one of the reacting substances per unit of time. Since the concentrations of the initial substances continuously diminish, the rate of change likewise continuously decreases; hence the working out of experimental results concerning rates of change involves the use of the calculus.[1]

Consider the reaction

$$m_1\text{A} + m_2\text{B} + m_3\text{C} + \ . \ . \ . \rightleftharpoons n_1\text{P} + n_2\text{Q} + n_3\text{R} + \ . \ . \ .$$

Denoting the concentrations[2] of A, B, . . ., at a time t after the commencement of the reaction by C_A, C_B, . . ., the velocity v of the forward change at that moment must be given by

$$v = k \,.\, C_A^{m_1} \,.\, C_B^{m_2} \,.\, C_C^{m_3} \ . \ . \ .,$$

where k denotes a constant called the *velocity constant*, the magnitude of which depends upon the units of time and volume chosen, and on the temperature. Similarly the velocity v' of the reverse change is given by

$$v' = k' \,.\, C_P^{n_1} \,.\, C_Q^{n_2} \,.\, C_R^{n_3} \ . \ . \ .,$$

where k' is the velocity constant for this reaction. At the time t, then, the observed rate of change will be $(v - v')$ in the forward direction. If the time t happens to be the time required for equilibrium to be reached, then at that moment, and subsequently, $v = v'$, *i.e.*

$$\frac{C_P^{n_1} \,.\, C_Q^{n_2} \,.\, C_R^{n_3} \ . \ . \ .}{C_A^{m_1} \,.\, C_B^{m_2} \,.\, C_C^{m_3} \ . \ . \ .} = \frac{k}{k'}.$$

The law of mass action is thus in harmony with the law of chemical equilibrium, and indicates that the equilibrium constant K (p. 171) is to be regarded as the ratio of two velocity constants.

The simplest type of change is an irreversible change in which only one molecular species is concerned and only one molecule is involved in the change. The rate of change is then expressed by

$$-\frac{dC}{dt} = kC,$$

where C denotes the concentration of the initial substance at any time t from the start. The integration of this equation gives

$$k = \frac{1}{t} \,.\, \log_e \frac{C_0}{C} = \frac{2{\cdot}303}{t} \log_{10} \frac{C_0}{C},$$

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[1] The reader desirous of familiarising himself with higher mathematics so far as is necessary to the study of physical chemistry may be recommended to Mellor, *Higher Mathematics for Students of Chemistry and Physics* (Longmans & Co., 2nd edition, 1905), or Partington, *Higher Mathematics for Chemical Students* (Methuen, 1911).

[2] In gram-molecules per unit of volume, as usual.

C_0 denoting the initial concentration. A method of expressing the result of integration which is sometimes preferable to the preceding is as follows:—

$$k = \frac{2{\cdot}303}{t_2 - t_1} \cdot \log_{10} \frac{C_1}{C_2},$$

C_1 and C_2 denoting the concentrations at times t_1 and t_2 respectively.

If, then, the concentration can be measured at various intervals of time from the start, simultaneous values of C and t can be inserted in these equations, and a series of values of k deduced. These values should be equal, within the limits of experimental error.

A change which proceeds in a manner described by the preceding equations is called a *unimolecular* change. An important characteristic of such changes may be pointed out at once. Suppose that a definite fraction, say $1/n$th, of the total quantity of original substance has undergone change. The concentration will have fallen to $(n-1)C_0/n$. The time required to effect this change is given by

$$t = \frac{2{\cdot}303}{k} \cdot \log_{10} \frac{nC_0}{(n-1)C_0} = \frac{2{\cdot}303}{k} \log_{10} \cdot \frac{n}{n-1}.$$

Hence the time required for any definite fraction of the initial substance to undergo change is independent of the concentration. From the kinetic point of view this result is quite intelligible, since each molecule decomposes on its own account, and the closeness or otherwise of neighbouring molecules is therefore of no consequence. It follows that "quantities of initial substance present" may be substituted for "concentrations" in the preceding equations.

The most interesting examples of inorganic changes which have been shown to follow the unimolecular law are the various *radioactive transformations*. Provided that a radioactive substance can be obtained in a homogeneous state and the products of its disintegration do not interfere, the rate of transformation, which may be measured by the rate of decay of radioactivity, follows the unimolecular law.[1] The velocity constants of these changes are called *radioactive constants*, and denoted by λ in the literature of the subject. It is also customary to state the "period of half change" T, by which is meant the time that must elapse after any particular moment, before the quantity of initial substance remaining is reduced to one-half the quantity present at that moment. From the preceding equation it is seen that

$$T = \frac{2{\cdot}303}{\lambda} \log_{10} 2 = 0{\cdot}693/\lambda.$$

The value of $1/\lambda$ is termed the period of average life of a radioactive element. In the case of radium F (or polonium) the period of half-change is 140 days. Hence, with the day as unit of time, the radioactive constant is $0{\cdot}693/140$ or $\cdot00495$, a result usually expressed as $\lambda(\text{day})^{-1} = 495 \times 10^{-5}$. Also, the period of average life is $1/0{\cdot}00495$ or 202 days.

It is quite possible for a reaction to follow the unimolecular law, *i.e.* give a good "constant" for k when the experimental data are inserted in the equation, even when the change must of necessity involve the interaction of at least two molecules. The classic example, in the study of which the law of mass action was used for the first time, is an organic reaction, the

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[1] Sometimes called the exponential law, since it may be written $C = C_0 . e^{-\lambda t}$.

"inversion" of sucrose in aqueous solution,[1] which proceeds according to the equation

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{levulose}}{C_6H_{12}O_6},$$

and gives a good "constant" for a unimolecular reaction, as the following results[2] serve to show :--

t, mins.	C, Arbitrary Units.	k.
0	10·023	...
30	9·022	0·00152
60	8·077	0·00156
90	7·253	0·00156
130	6·297	0·00155
180	5·347	0·00151

In this reaction the medium (water) participates in the change. In all such reactions the concentration of the medium only changes by an inappreciable fraction of its initial value, and may therefore be regarded as a constant. Hence the only change of concentration that is of any consequence in the preceding case is that of the sugar.

A chemical change that proceeds by the interaction of two molecules is said to be *bimolecular*. Denoting the two substances by A and B, the equation

$$-\frac{dC_A}{dt} = k \, . \, C_A \, . \, C_B$$

holds for the rate of change. Only the simple case when initially C_A is equal to C_B will be considered. In this case

$$-\frac{dC}{dt} = kC^2;$$

whence, by integration,

$$k = \frac{1}{t_2 - t_1} \, . \left(\frac{1}{C_2} - \frac{1}{C_1}\right),$$

a result which is in a form suitable for the testing of experimental data.

The conversion of ozone into oxygen is, at 100°, an irreversible change which follows the bimolecular law.[3] The change thus appears to be expressed by the equation

$$2O_3 = 3O_2.$$

Its progress is readily observed by measuring the rate of increase of pressure within the system, maintained at constant volume.

The decomposition of hydrogen iodide by heat—

$$2HI \rightleftharpoons H_2 + I_2,$$

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[1] Wilhelmy, *Pogg. Annalen*, 1850, **81**, 413, 499; Ostwald's *Klassiker*, No. 29.

[2] Quoted from Mellor, *Chemical Statics and Dynamics* (Longmans & Co., 1904), p. 40.

[3] Clarke and Chapman, *Trans. Chem. Soc.*, 1908, **93**, 1638; Chapman and Jones, *ibid.*, 1910, **97**, 2463; Chapman, *Science Progress*, 1911-2, **6**, 438.

is a reversible reaction in which both the forward and the reverse changes are bimolecular. For the velocity of reaction the equation

$$-\frac{dC_{HI}}{dt}=kC_{HI}^2-k'.C_{H_2}.C_{I_2}$$

holds good. If the reaction be started with pure hydrogen iodide at a concentration C_0, and the concentration has fallen to C after a time t, the concentration of hydrogen is equal to $(C_0-C)/2$, and that of iodine is the same. Hence,

$$-\frac{dC}{dt}=k'\left(\frac{k}{k'}C^2-\frac{(C_0-C)^2}{4}\right).$$

The ratio k/k' is equal to the equilibrium constant K, and can therefore be determined experimentally and its value inserted in the equation. The integration, which is quite simple, leads to an expression for k' in terms of C, C_0, and t, and experiment has shown that the expression actually has a constant value during the experiment.[1]

In a bimolecular change the time required for a definite fraction of the original substances (taken in equivalent proportions) to be transformed is inversely proportional to the initial concentration. The proof may be left to the reader.

Few changes are known which involve the direct interaction of three or more molecules, and they will not be discussed here. Their rarity is readily understood from the point of view of the kinetic theory. It therefore appears that complicated reactions take place in successive stages, and the fact that a complicated change follows the law for a bimolecular or termolecular reaction may be explained by supposing that one of the stages is of that order, and that all the other stages have velocity constants exceedingly large in comparison with that particular stage. To take quite a simple case, the decomposition of hydrogen peroxide in aqueous solution proceeds as a unimolecular change. According to the equation

$$2H_2O_2=2H_2O+O_2,$$

it would be expected to be bimolecular. Hence it is supposed that two successive reactions occur:—

(i.) $H_2O_2=H_2O+O$ (unimolecular)
(ii.) $2O=O_2$

and that (ii.) proceeds at a rate enormously greater than (i.).

All chemical changes the velocities of which have been measured do not exhibit the simplicity that might be anticipated from the foregoing account. The "irregularities" often observed may at times be traced to definite causes. One of the products of a change may, as soon as it is formed, commence a reaction with one or other of the initial substances; or the initial substances may be capable of interacting in a number of ways, and accordingly two or more independent changes may proceed simultaneously. In either of these circumstances "side reactions" are said to occur. The existence of a *period of induction* is observed at the commencement of various reactions. During such a period the velocity increases to a maximum, afterwards falling off in the normal manner. It is not difficult to show that the existence of a period of induction is a consequence of the Law of Mass Action if the change in question proceeds in successive stages, but that the detection of the phenomenon[1] is very improbable unless the velocity constants for the successive stages are of about the same order of magnitude, the greatest not being more than, say, ten times the smallest. It must not be concluded, however, that the observation of a period of induction proves that a change proceeds in stages. The most interesting period of induction is that observed when chlorine and hydrogen unite under the influence of a feeble light—a reaction which is termed a *photochemical* change. The existence of this period of induction has been known for years, but it is only within recent times that it has been shown that the pure gases do not exhibit the phenomenon, which is due to the presence of minute quantities of nitrogenous impurities which prevent the formation of hydrogen chloride, and which are themselves destroyed by light.[2]

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[1] See Van't Hoff, *Lectures on Theoretical and Physical Chemistry*, translated by Lehfeldt (Arnold, 1899), vol. i. p. 187.

The radioactive transformations afford beautiful illustrations of *successive unimolecular changes.* For example, radium is transformed by loss of α-particles into niton, or radium emanation, which in turn loses α-particles and changes into radium A. The latter spontaneously changes into radium B, and so on, radium F eventually passing with loss of α-particles into an inactive product which is probably lead. The periods of half-change of these successive transformations vary enormously, being as follows:—

$$\begin{array}{ccccccccccccc} & & & & & & & & \text{radium } C_1 & & & \\ \text{radium} & \rightarrow & \text{niton} & \rightarrow & \text{radium A} & \rightarrow & \text{radium B} & \rightarrow & 19{\cdot}5 \text{ mins.} & \rightarrow & \text{radium D} & \rightarrow \\ c.\ 1700 & & 3{\cdot}86 \text{ days} & & 3 \text{ mins.} & & 26{\cdot}7 \text{ mins.} & & \text{radium } C_2 & & c.\ 17 \text{ years} & \\ \text{years} & & & & & & & & 1{\cdot}38 \text{ mins.} & & & \end{array}$$

$$\begin{array}{ccccc} \text{radium E} & \rightarrow & \text{radium F} & \rightarrow & \text{radium G} \\ 5{\cdot}1 \text{ days} & & 140 \text{ days} & & \text{not radioactive.} \end{array}$$

Heterogeneous Systems.—It is not proposed to discuss here the results that have been obtained in studying velocity of reaction in heterogeneous systems. One or two remarks only can be made. It will be obvious that the observed rate of change in such systems must be largely influenced by the extent of the surfaces of separation between the phases, and hence, for example, the rate of solution of calcium carbonate in hydrochloric acid will depend upon the state of division of the solid. Further, such velocities are dependent upon the rate at which the products of reaction diffuse away from the surfaces of separation, and hence, in the case just quoted, the velocity will vary if the liquid is stirred at different rates. It is probable that in many reactions the change proceeds with great rapidity where the phases come into contact, and that the observed rates of change are determined almost exclusively by diffusion velocities.[3]

Various reactions must be regarded as taking place in heterogeneous systems, although at first sight this may not seem to be the case. The union of hydrogen and oxygen, the rate of which can be measured at suitable temperatures, is a case in point. The reaction takes place almost exclusively at the walls of the enclosing vessel, and when the latter is packed with porous porcelain the velocity of reaction appears to depend largely upon the rate of adsorption of hydrogen by the porcelain surface.[1] The decomposition of phosphine, arsine,[2] and stibine[3] into their elements when heated afford further examples, the decomposition taking place in the layer of gas adsorbed by the surface of the containing vessel. The fact that the first two of these reactions appear to be unimolecular changes[4] probably means that the rate of adsorption of gas by the surface is proportional to the pressure.

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[1] *E.g.*, by observing that a satisfactory velocity constant is not obtained in the initial stages of the reaction.

[2] Burgess and Chapman, *Trans. Chem. Soc.*, 1906, **89**, 1399; Chapman, *Science Progress*, 1911–2, **6**, 657; 1912–3, **7**, 66; see also Vol. VIII. of this series.

[3] Nernst, *Zeitsch. physikal. Chem.*, 1904, **47**, 52.

Influence of Temperature and Medium on Rate of Change.—In the case of the radio-active transformations, the velocity constants appear to be quite independent of the temperature. With all other changes, however, a change of temperature affects the velocity of reaction, and with one or two exceptions a rise of temperature causes the change to proceed at a greater rate than before. In homogeneous systems, the velocity constant is usually doubled or trebled by a rise in temperature of ten degrees, and so an increase of temperature of one hundred degrees generally increases the velocity constant at least a thousandfold. It is accordingly easy to understand why comparatively few reactions lend themselves to velocity measurements at temperatures convenient for experimental work. At ordinary temperatures many reactions, particularly those between acids, bases, and salts, proceed far too rapidly for their velocities to be measured. On the other hand, many reactions must be considered as progressing at the ordinary temperatures, although at such slow rates that no observable change occurs in any reasonable period of time. Thus, a mixture of hydrogen and oxygen must be regarded, at ordinary temperatures, as changing, although excessively slowly, into the more stable system in which practically all the gases are united in the form of water; and observations extending over a number of years actually show that yellow phosphorus slowly changes into the more stable red form. Some reactions can occur with great velocity at very low temperatures. For example, fluorine and hydrogen unite with violence at −252·5°, and fluorine will react spontaneously with sulphur, arsenic, and other elements at −187°.[5]

The remarkable influence of temperature on rate of change is often applied with advantage in investigating states of equilibrium. Since, for example, neither the decomposition of hydrogen iodide nor the reverse change proceeds at an appreciable rate at the ordinary temperature, it is possible to determine the quantities of hydrogen iodide, iodine, and hydrogen present in a system in equilibrium at a high temperature by cooling the system with great rapidity, and then applying the methods of chemical analysis to the problem.

From the nature of Van't Hoff's equation connecting displacement of equilibrium with change of temperature, it follows, on the dynamic view of equilibrium, that the connection between temperature and velocity constant for a homogeneous change is of the form

$$\frac{d}{dT}\log_e k = \frac{A}{T^2} + B,$$

where B is independent of, but A varies somewhat with the temperature (since A depends upon the value of the heat of reaction). The majority of the empirical formulæ that have been found to represent satisfactorily the influence of T upon k in particular reactions can be derived from the preceding equation by assuming that A varies with T in a suitable, generally quite a simple, manner.

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[1] Bone and Wheeler, *Phil. Trans.*, 1906, **206**, 1.

[2] Van't Hoff and Cohen, *Studies in Chemical Dynamics*, translated by Ewan (Williams & Norgate, 1896), pp. 1 and 49

[3] Stock and Bodenstein, *Ber.*, 1907, **40**, 570.

[4] Van't Hoff and Cohen, *opus cit.*

[5] Moissan and Dewar, *Compt. rend.*, 1903, **136**, 641, 785.

The view here expressed concerning the influence of temperature upon rate of change may be stated in the form that the velocity of a reaction changes continuously with change of temperature; but there is a number of changes in which this view appears to be incorrect. For a discussion of such changes, and the nature of "false equilibrium," however, the reader must be referred elsewhere.[1]

A change in the nature of the medium influences the rate of progress of a chemical reaction often to an enormous extent. For example, the slow decomposition of carbon oxysulphide in aqueous solution,

$$COS + H_2O = CO_2 + H_2S,$$

is an example of a bimolecular change which gives a good constant for a unimolecular reaction (see p. 183). At constant temperature the velocity constant for this change is considerably altered when the nature of the medium is altered by the addition of a soluble acid or salt.[2] A most striking instance is furnished by Menschutkin's determination of the rate of combination of triethylamine $(C_2H_5)_3N$ and ethyl iodide C_2H_5I at 100° in various organic solvents.[3] With hexane as solvent the velocity constant for this bimolecular change is 0·00018, whilst with benzyl alcohol it is 0·133. The influence of the solvent upon the degree of molecular complexity of a solute (see Chap. IV.) may also be mentioned. An equilibrium is involved in all such cases, and the rates of the opposing reactions are unequally influenced by change of solvent. In the decomposition of ozone[1] at 100°, interesting as being the only case of irreversible homogeneous change in the gaseous state at present (1914) known, the presence of oxygen, nitrogen, carbon dioxide, or water vapour, has no effect, the rate of change being conditioned solely by the concentration of ozone in the mixture.

A satisfactory explanation of the influence of the medium is still lacking.

Catalysis.—It has been already pointed out that the rate at which a reaction proceeds is changed by altering the medium in which it takes place. Frequently, however, it is noticed that the rate is altered, usually greatly increased, in the presence of a very small quantity of a "foreign" substance, that is to say, a substance that apparently takes no part in the change and is left at the completion of the change unaltered in chemical composition and in quantity. The foreign substance is called a *catalyst* or *catalytic agent*, and the phenomenon is termed *catalysis*. Examples are very numerous. The evolution of oxygen by heating potassium chlorate proceeds at about 400°, but when a little manganese dioxide is added, oxygen can be readily obtained at temperatures a little over 200°, before even the chlorate melts. The rate of union of hydrogen and oxygen, hydrogen and iodine, and sulphur dioxide and oxygen is in each case greatly accelerated by contact with spongy platinum. The addition of a little colloidal platinum brings about the rapid decomposition of hydrogen peroxide in aqueous solution at the ordinary temperature. The "inversion" of sucrose only proceeds with appreciable velocity in the presence of acid, which is left undiminished in quantity at the end of the experiment, etc.

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[1] Mellor, *opus cit.*

[2] Buchbock, *Zeitsch. physikal. Chem.*, 1897, **23**, 123; 1900, **34**, 229.

[3] Menschutkin, *Zeitsch. physikal. Chem.*, 1890, **6**, 41. For other examples see Dimroth, *Annalen*, 1910, **377**, 127; Segaller, *Trans. Chem. Soc.*, 1914, **105**, 112.

[4] *Vide supra*, p. 184.

A catalyst is defined by Ostwald as a substance which changes the velocity of a reaction without itself being changed by the process, a definition which implies that a catalyst is incapable of starting a reaction, and only affects the speed of a reaction already proceeding, though perhaps at an exceedingly slow rate. This is, however, in the present state of knowledge, only a matter of opinion, and others hold that a catalyst can actually initiate a reaction. The quantity of a catalyst present is often excessively small in comparison with the quantity of material reacting. For instance, ten litres of a mixture of hydrogen and oxygen were caused to combine at the ordinary temperature in the presence of 0·0004 gram of colloidal platinum, and the activity of the catalyst was still unimpaired.[1] The final state of a system undergoing change must therefore be independent of the nature and quantity of any catalyst present, and, in particular, the state of equilibrium in a reversible change cannot be affected by a catalyst.[2] For instance, it has been shown at 350° and in the absence of a catalyst, hydrogen iodide decomposes to the extent of 18·6 per cent. before equilibrium is reached,[3] while in the presence of platinum black as catalyst 19 per cent. was found to have dissociated.[4] Hence it follows that a catalyst which modifies the forward rate of change in a reversible reaction must similarly modify the rate of progress of the reverse change, a conclusion that is in harmony with experiment.

The enormous influence of water vapour on many chemical changes affords numerous striking instances of catalysis. Carbon monoxide does not combine with oxygen under the influence of the electric spark when the mixed gases are perfectly dry.[5] A similar result is observed with dry hydrogen and oxygen. Numerous elements are unchanged when heated in dry oxygen or chlorine; thus sodium may be melted in dry oxygen without chemical change occurring. Dry ammonia and hydrogen chloride do not unite, and, conversely, dry ammonium chloride does not dissociate when heated. The dissociation of calomel vapour into mercury and mercuric chloride does not occur with the dry substance, and dry nitrogen trioxide vapour, far from being dissociated into peroxide and nitric oxide, is largely associated as N_4O_6 molecules.[6]

It is not possible to say with certainty whether these reactions are actually stopped by the absence of moisture, or whether the changes still proceed with exceedingly small velocities. It has been supposed that two perfectly pure substances cannot react, the presence of a third being essential to the commencement of chemical change;[7] but the difficulty of proving such an hypothesis experimentally is obvious, and as a general theory of chemical change this view is not widely accepted.

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[1] Ernst, *Zeitsch. physikal. Chem.*, 1901, **37**, 448.

[2] Owing to the difficulty of defining exactly the nature of catalysis, this conclusion is open to question. Thus, it is difficult to see how the "influence of the solvent," referred to in the preceding section, can be excluded from what is termed catalysis, if the usual definition is accepted, and yet change of solvent is associated with displacement of equilibrium.

[3] Lemoine, *Ann Chim. Phys.*, 1877, (v.), **12**, 145.

[4] Hautefeuille, *Compt. rend.*, 1867, **64**, 608.

[5] Dixon, *Brit. Assoc. Reports*, 1880, 593.

[6] For full references to the literature of this phase of the subject, see Mellor and ~~Russell~~, *Trans. Chem. Soc.*, 1902, **81**, 1272; Baker, *ibid.*, 1894, **65**, 611; 1907, **91**, 1862.

[7] Armstrong, *Trans. Chem. Soc.*, 1886, **49**, 112; 1895, **67**, 1122; 1903, **83**, 1088; *Proc. Roy. Soc.*, 1886, **40**, 287; 1902, **70**, 99; 1904, **74**, 86.

Many chemical processes carried out on a manufacturing scale are hastened by catalysts;[1] for instance, the manufacture of sulphuric acid by the chamber process, of sulphur trioxide by the contact process, of chlorine by Deacon's process, etc., and catalysis is therefore a subject of great practical as well as theoretical importance. No satisfactory general theory of catalysis is at present known,[2] and probably the many instances of catalytic action known cannot all be explained on the same hypothesis. The favourite mode of explanation is to assume the formation of *intermediate compounds*, into the compositions of which the catalysts enter;[3] these intermediate substances then react to yield the final products and regenerate the catalysts. Particular instances in which this view receives experimental support will be dealt with as occasion arises in the other volumes of this series of text-books.[4]

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[1] See Jobling, *Chemical World*, 1914; Conroy, *J. Soc. Chem. Ind.*, 1902, **21**, 302, where numerous cases are discussed.

[2] A promising theory of homogeneous catalysis has been outlined by Rosanoff (*J. Amer. Chem. Soc.*, 1913, **35**, 173). See also Rosanoff and Potter, *ibid.*, 1913, **35**, 248.

[3] In which case it may very well happen that the catalyst *actually brings about* a reaction, and not merely hastens one already in progress.

[4] For further information, *vide* Mellor, *opus cit.* (p. 169); Ostwald, *Ueber Katalyse* (Leipzig, 1902).

CHAPTER VI.

ACIDS, BASES, AND SALTS.

Historical.—The only acid with which the ancients were familiar was *vinegar.*[1] They noted that it acted as a solvent upon many substances, dissolving calcareous earth, for instance, with effervescence. Subsequently, other liquids were prepared, characterised by similar solvent powers and possessed of a sour taste, and they were classed together as *acids.* Impure nitric and sulphuric acids were known in the eighth century. The alchemists attached considerable importance to acids, and regarded their power of dissolving substances which are insoluble in water as their distinguishing characteristic.

The name *alkali*[2] was originally applied to the ashes of sea plants, the detergent properties of which were noticed in very early times. Later, the application of the term was extended to include other substances, which, like the original alkali, dissolved in water, producing solutions having a soapy action on the skin and the power of affecting the colour of various plant pigments.

The interactions of acids and alkalis were much studied during the seventeenth century. It was noticed that the substance produced when an acid and an alkali were mixed did not exhibit the characteristic properties of either an acid or a base; such substances became known as *salts.* Boyle[3] pointed out that acids were characterised by solvent power, the ability to precipitate sulphur from its solution in alkalis, the power of turning certain blue vegetable colouring-matters red (alkalis effecting the reverse change) and of combining with alkalis, when a salt was produced. A number of alkalis were noticed to effervesce with acids, and were called *mild alkalis* to distinguish them from the others, or *caustic alkalis.* Further, substances were discovered which, although practically insoluble in water, nevertheless combined with acids to form salts. These were called *earths,* being further distinguished as *mild earths* when their interaction with acids was accompanied by effervescence.

Originally the word *salt* was applied to sea salt, and even at the present day it is still commonly employed with this meaning. Subsequently the term *salt* came into use as a class name for substances which, like sea-salt, are soluble in water and may be recovered from the solution by evaporation of the solvent. Paracelsus (sixteenth century) and the iatrochemists applied the term to denote solid substances obtained by the combustion or ignition of other substances. Early in the eighteenth century the special properties of salts were stated by Boerhaave[1] to be solubility, fusibility or volatility, and taste. Later, however, the acids and alkalis were exempted from this definition, while insoluble, tasteless substances obtained by the interaction of certain earths and acids were classed as salts, so that the term "salt" came to include all substances produced by the action of acids on alkalis, earths, metals, and calces of metals (*i.e.* substances obtained by heating the metals in air).[2] Substances which formed salts by interaction with acids were grouped together as *bases* by Rouelle in 1744.

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[1] Greek ὀξύς, Latin *acidus* = sour; Greek ὄξος, Latin *acetus* – vinegar.

[2] Arabian = the ash.

[3] Boyle's *Collected Works* (1772), vol. iv. p. 284.

Van Helmont distinguished between fixed alkali and volatile alkali (ammonia); in 1736 Duhamel divided fixed alkali into vegetable (potash) and mineral alkali (soda). For a long time it was supposed that the caustic alkalis and the earths were more complex than the mild alkalis and mild earths; for example, following the views of "Basil Valentine," limestone, which effervesced with acids, was supposed to combine with "matter of fire" when heated, thereby producing quicklime, which did not effervesce with acids. It was, however, shown by Black,[3] that limestone is really quicklime combined with a peculiar gas which differs from ordinary air, and that it is this gas, called *fixed air* by Black, which escapes when limestone dissolves in an acid with effervescence. He further showed that the mild earth "magnesia alba" is similarly related to magnesia, since it consists of magnesia combined with fixed air; and that the same product is obtained in solution, whether magnesia or magnesia alba be dissolved in an acid. The work of Black enabled a clear distinction to be drawn between mild and caustic alkalis and between the earths and mild earths.

The discovery of oxygen by Priestley[4] and Scheele,[5] and the recognition of the real nature of the phenomenon of combustion by Lavoisier[6] in 1777, led to the *oxygen theory* of acids. From the fact that various non-metals, *e.g.* carbon, sulphur, and phosphorus, combine with oxygen to form oxides[7] which dissolve in water yielding acid solutions, Lavoisier concluded that oxygen was the "acidifying principle" and was contained in all acids. To him an acid was a combination of oxygen with an "acidifiable base,"[8] which was usually a non-metal; the oxides of the metals were not acids, but were identical with the calces obtained by heating the metals in air. Although it was subsequently shown that certain acids do not contain oxygen, the idea that most acids were oxides was generally held until about 1838, and the compounds that these oxides were known to form with water were regarded as hydrates of the acids.

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[1] Boerhaave, *Elementa Chemiæ*, 1732.

[2] See Lavoisier, *Elements of Chemistry*, translated by Kerr, 4th edition, 1799; Nicholson, *The First Principles of Chemistry*, 1st edition, 1790, 3rd edition, 1796.

[3] Black, *Experiments on Magnesia Alba, Quicklime, and other Alcaline Substances*, 1755; *Alembic Club Reprints* (Clay, 1893), No. 1.

[4] Priestley, *Experiments and Observations on Different Kinds of Air*, 1775; *Alembic Club Reprints* (Clay, 1894), No. 7.

[5] Scheele, *Chemical Treatise on Air and Fire*, 1777; *Alembic Club Reprints* (Clay, 1894), No. 8.

[6] Lavoisier, *Œuvres*, vol. ii. p. 206.

[7] Binary compounds containing oxygen are called *oxides*; those containing sulphur, *sulphides*; selenium, *selenides*; tellurium, *tellurides*; hydrogen, *hydrides*; chlorine, *chlorides*; bromine, *bromides*; iodine, *iodides*; fluorine, *fluorides*; nitrogen, *nitrides*; phosphorus, *phosphides*, etc. The suffix *-ide* almost invariably terminates the name of a *binary* compound; and the name modified is that of the more *negative* element, *e.g.* ZnO, *zinc oxide*; NaCl, *sodium chloride*, etc.

[8] Also called the *radicle*, a term due to G. de Morveau. For the history of the various meanings that have been assigned to the word *radicle* see Ladenburg, *Lectures on the History of Chemistry*, translated by Dobbin, (Thin, 1905), Lectures 7 and 8.

Salts were regarded by Lavoisier and his followers as compounds of acids and bases, the latter including calces or metallic oxides, caustic alkalis, and earths. Although he was unable to prove it, Lavoisier was inclined to regard the earths as being oxides of metals, and this view was shortly afterwards confirmed. In 1807 Davy[1] isolated the metals sodium and potassium by the electrolysis of fused soda and potash respectively, the metals appearing at the cathode, and oxygen at the anode. He accordingly regarded the alkalis as oxides of these metals (later they were shown to be hydroxides), and, turning his attention to the earths, he succeeded in showing that lime, strontia, baryta, and magnesia were oxides of hitherto unknown metals, which he isolated in an impure state.[2]

Lavoisier's theory of the constitution of salts was developed by Berzelius[3] into the *dualistic theory* of chemical combination, an electrochemical theory which dominated chemistry for many years. According to Berzelius, each chemical atom, when in contact with another, is electrified. Each atom possesses two poles, a positive and a negative pole; but the charge at one pole is much greater than that at the other pole, and consequently an atom appears to be either positively or negatively charged according as to which of its poles carries the greater charge. The most electronegative element, according to Berzelius, was oxygen. In chemical combination between two elements there is a neutralisation of opposite electricities, accompanied by manifestations of heat and light. For instance, in the union of oxygen and another element, there is a partial neutralisation of negative electricity from the oxygen, and positive electricity from the other element; but as the positive charge on the one element may be greater or less in quantity than the negative charge on the second, the compound produced possesses a certain residual charge of negative or positive sign. The "compound of the first order" so produced is hence capable of still further combination; the oxide of potassium, for example, which is positive, can unite with the oxide of sulphur (or sulphuric acid, as it was called), which is negative, to form sulphate of potash, a "compound of the second order." This, in like manner, is still capable of combination, for example, with sulphate of alumina to form alum; but, according to Berzelius, the stronger poles in general are neutralised first, and so the intensities of the electric forces, to which chemical combination is to be attributed, diminish the higher the order of the compound becomes.

On this dualistic view, then, every compound was supposed to be capable of division into two parts, one positively and the other negatively electrical. A salt was regarded as a compound of the second order, formed by the union of a positive metallic oxide and an acid or negative oxide, each of the oxides being a compound of the first order; and formulæ were written in such a manner as to indicate this idea. Sulphate of potash, for example, a compound of potassium oxide, KO, and sulphuric acid, SO_3, was written $KO.SO_3$.

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[1] Davy, *Phil. Trans.*, 1808, 98, 1.

[2] Davy, *Phil. Trans.*, 1808, 98, 333.

[3] Berzelius, *Schweigger's Journal*, 1812, 6, 119; *Lehrbuch der Chemie* (Dresden, 2nd edition, 1827), vol. iii. part 1.

Lavoisier's view that all acids must contain oxygen was generally accepted by his contemporaries; but Berthollet, in 1787, expressed a different opinion. He pointed out that prussic acid contains carbon, hydrogen, and nitrogen only, and that sulphuretted hydrogen, which behaves as an acid, contains nothing but sulphur and hydrogen. Accordingly, he regarded other elements besides oxygen as acid-producing; but few chemists accepted his views. Between the years 1808–10, however, it was demonstrated by Davy[1] that chlorine, discovered in 1774 by Scheele,[2] is an elementary substance, and that it combines with hydrogen to form a compound which behaves in solution as a strong acid. It had previously been assumed that chlorine contained oxygen, and Gay-Lussac and Thenard,[2] who studied the reactions of chlorine and its hydrogen compound about the same time as Davy, adopted the view that hydrochloric acid was a compound of an unknown radical *muriaticum* with oxygen and water. Gay-Lussac, however, eventually accepted Davy's view, being led to this step both by his investigation of the properties of iodine, during the course of which he prepared hydriodic acid,[3] and by his study of prussic acid and cyanogen.[4] The experiments of Davy and Gay-Lussac made it impossible to assume any longer that oxygen was a constituent of all acids. The acids devoid of oxygen were called *hydracids* by Gay-Lussac, and Berzelius drew a sharp distinction between, on the one hand, the *hydracids* and their salts, the *haloid salts*; and, on the other hand, the *oxyacids* and their salts, the *amphid salts*.

The modern, or *hydrogen theory* of acids followed quickly after the discovery of the polybasic acids. The latter is due to the classical investigations of Graham in 1833.[5] Graham showed that the water contained in "hydrated acids" was essential to their constitution, and that ordinary phosphoric acid is to be regarded as a compound of one "atom" of phosphoric oxide, and three "atoms" of water. The salts of the acid are likewise to be looked upon as compounds of one "atom" of phosphoric oxide and three "atoms" of base, of which one or two "atoms" may be water—*i.e.* the salts are derived by the partial or complete replacement of the three "atoms" of water in the acid by "atoms" of base. He further showed that there are two other phosphoric acids, one of which is a compound of one "atom" of phosphoric oxide and two "atoms" of water, while the other is a compound of one "atom" of phosphoric oxide and one "atom" of water; and that the salts of these acids are likewise derived by the replacement of the "atoms" of water by "atoms" of base. Thus, Graham showed that what was at that time regarded as phosphoric acid formed three distinct hydrates, which were able to saturate different quantities of base.

In 1838 Liebig[6] showed that a large number of organic acids resemble phosphoric acid. For example, tartaric acid not only forms salts by the replacement of one atom of water by one atom of base, but it also forms salts by the replacement of two atoms of water by two atoms of either the same base or different bases. Thus arose the idea of *polybasic acids*. But Liebig went further than this; he showed how to get rid of the division of acids into hydracids and oxyacids.

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[1] *Alembic Club Reprints* (Clay, 1894), No. 9.

[2] *Alembic Club Reprints* (Clay, 1897), No. 13.

[3] Gay-Lussac, *Ann. Chim.*, 1814, **91**, 5.

[4] Gay-Lussac, *Ann. Chim.*, 1815, **95**, 136.

[5] Graham, *Phil. Trans.*, 1833, **123**, 253; *Alembic Club Reprints* (Clay, 1895), No. 10.

[6] Liebig, *Annalen*, 1838, **26**, 113.

According to the dualistic view of the nature of salts, it was necessary to explain the formation of a haloid salt by a process different from that which was assumed to account for the production of an amphid salt. For example, whereas iron was supposed merely to replace hydrogen in hydrochloric acid, with the formation of ferrous chloride, it was necessary to suppose that in the production of ferrous sulphate from iron and sulphuric acid, the presence of the acid SO_3 enabled the iron to decompose the water, forming ferrous oxide and liberating hydrogen, and that the oxide then united with the acid to form $FeO.SO_3$. The two reactions, however, are similar in character, and Liebig put forward a theory of the nature of acids in which this similarity finds a ready expression.

According to Liebig, what had previously been regarded as hydrates of acids are the real acids. The acids, in fact, are hydrogen compounds, in which part or all of the hydrogen may be replaced by metals, with the formation of salts.[1] The nature of an acid is therefore expressed by the statement—

$$\text{acid} = \text{replaceable hydrogen} + \text{acid radicle},$$

by "acid radicle" being understood the remaining constituents of the acid. For example, sulphuric acid H_2SO_4 consists of replaceable hydrogen H_2 and acid radicle SO_4. The two reactions just mentioned—namely, the formation of ferrous chloride and ferrous sulphate—are similar in character, in each case hydrogen of the acid being replaced by metal. The formation of these salts from the ferrous oxide and the acids is likewise a case of similar reactions,

$$FeO + 2HCl = FeCl_2 + H_2O,$$
$$FeO + H_2SO_4 = FeSO_4 + H_2O,$$

in each case the reaction being

$$\text{oxide of metal} + \text{acid} = \text{salt} + \text{water}.$$

Liebig's view is essentially that which is held to-day, acids and salts being regarded as strictly analogous. This is well borne out by the study of electrolysis, which will be discussed in some detail later on in this chapter.

Acids.—Without attempting to define exactly what is understood by an acid, it may be said that an acid is a compound of hydrogen, which in solution is capable of exchanging part or all the hydrogen (the "acidic" hydrogen) it contains for a metal, with the simultaneous formation of water, by the action of a metallic oxide or hydroxide on the solution.

Although hydrogen is the essential constituent of an acid, most acids contain oxygen as well.[2] The chief exceptions are the hydracids or compounds of hydrogen with the halogens and with cyanogen, such acids as

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[1] This view had been previously expressed by Davy, *Phil. Trans.*, 1811, 101, 155; 1815, 105, 219; *Alembic Club Reprints* (Clay, 1891), No 9, p. 63, and by Dulong in 1815.

[2] It frequently happens that several acids are known, closely related in composition, being, in fact, compounds of the same elements, but differing in the amounts of oxygen they contain relatively to the other elements. In naming these acids a systematic method is employed. The name of one acid is chosen to end in *-ic*, and the suffix *-ous*, and the prefixes *hypo-* and *per-* employed in the manner indicated in the following example:—

$HClO$	*hypo*chlor*ous* acid.
$HClO_2$	chlor*ous* ,,
$HClO_3$	chlor*ic* ,,
$HClO_4$	*per*chlor*ic* ,,

fluosilicic acid, $2HF.SiF_4$ or H_2SiF_6, and the thio-acids, such as thio-carbonic acid, H_2CS_3, which are analogous to oxyacids, but contain sulphur in place of oxygen.

An acid is said to be *mono-*, *di-*, *tri-*, etc., *basic*, according as its molecule contains one, two, three, etc., atoms of hydrogen replaceable by metals. Besides forming so-called *normal* salts in which metal replaces all the acidic hydrogen, polybasic acids are capable of forming salts in which only part of the hydrogen is so replaced. These intermediate derivatives are called *acid salts*. Since sodium and potassium salts are derived from acids by the replacement of hydrogen for metal, atom for atom, the basicity of an acid is equal to the number of sodium or potassium salts that it forms. For example, phosphoric acid, H_3PO_4, yields three potassium salts, having the formulæ

$$KH_2PO_4, \quad K_2HPO_4, \quad \text{and} \quad K_3PO_4,$$

and hence is tribasic. The first two salts are acid salts, but the third is the *normal* salt, *i.e.* the salt derived by the replacement of all acidic hydrogen in the acid by metal.

The basicity of an acid cannot be determined by mere inspection of the molecular formula. Hypophosphorous acid, H_3PO_2, for instance, might in that way be considered tribasic, whilst actually it is monobasic and yields only one potassium salt KH_2PO_2.

Information concerning the basicities of acids may be derived from thermochemical measurements. A monobasic acid forms only one sodium salt, and accordingly the heat evolved when a dilute aqueous solution of one gram-molecule of the acid is neutralised by a dilute solution of x gram-molecules of sodium hydroxide is practically independent of x for values of x starting from unity and increasing; the heat evolved is, however, very nearly proportional to x for values of x less than unity. This is illustrated by the numbers given in the following table:—

Acid.	No. of gram-molecules of NaOH added to one of acid.		
	$\frac{1}{2}$.	1.	2.
	Cals.	Cals.	Cals.
HCl, HBr or HI .	6·85	13·7	13·7
H_2S . .	3·9	7·7	7·7
HCN . . .	1·4	2·8	2·8
H_3PO_2 . . .	7·7	15·2	15 2
HNO_3 . . .	6·8	13·7	13·6

On the other hand, if, in a series of experiments, the gram-molecule of a polybasic acid in dilute solution is mixed with 1, 2, 3 . . . n gram-molecules of sodium hydroxide successively, the quantities of heat liberated at first increase, but at length become practically equal. If the evolution of heat is practically unchanged when the number of gram-molecules of sodium hydroxide is increased beyond m, the acid is m-basic. Examples are given in the accompanying table in which the heat unit is the kilogram-calorie or Cal. :—

Acid.	No. of gram-molecules of NaOH to one of acid.						Basicity of Acid.
	½.	1.	2.	3.	4.	6	
H_2SO_4 . . .	7·1	14·6	31·0	...	31·2	..	2
H_2SO_3 . . .	...	15·9	29·0	...	29·2	...	2
H_3PO_3 . . .	7 5	14·8	28·4	28·8	.	...	2
H_3PO_4 . . .	7·4	11·8	27·0	33·9	...	35·4	3
$H_4P_2O_7$ . . .	...	14·4	28 6	.	52·8	54·6	4

The results obtained in this manner do not always agree with those derived from a study of the compositions of the metallic salts. Hydrogen sulphide, for example, is dibasic, but the thermochemical method indicates a basicity of unity. The reason is that sodium sulphide, Na_2S, is hydrolysed almost completely in dilute aqueous solution thus—

$$Na_2S + H_2O \rightleftharpoons NaHS + NaOH,$$

and hence the thermal change when two gram-molecules of alkali are added to one of hydrogen sulphide differs inappreciably from that observed when only one gram-molecule of alkali is used.

Oxides.[1]—The oxides may be divided into various classes according to their chemical behaviour.

An oxide which combines with water to form an oxyacid is called an *anhydride* or *acidic oxide*. For example, sulphur trioxide is the anhydride of sulphuric acid—

$$H_2O + SO_3 = H_2SO_4,$$

and hence is often called sulphuric anhydride. One or two oxides may be called anhydrides in a certain sense, because they may be obtained from oxyacids by loss of water, although they do not unite with water to form the acid. Thus nitrous oxide may be looked upon as hyponitrous anhydride, since the change—

$$H_2N_2O_2 = N_2O + H_2O,$$

can be realised, but not the reverse change.

Most anhydrides are oxides of non-metals or metalloids, but they include one or two metallic oxides. These are invariably the higher oxides of the metals, *i.e.* those containing the greatest amount of oxygen. Examples are chromic anhydride CrO_3 and permanganic anhydride Mn_2O_7.

An oxide that reacts with an acid to produce a salt and water only is called a *basic oxide*. Examples are numerous; calcium oxide, CaO, ferrous oxide, FeO, ferric oxide, Fe_2O_3, etc.[2] They are oxides of metals (or metalloids), the oxides of non-metals not being basic.

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[1] When an element forms a number of oxides, numerical prefixes are often used in naming the compounds in order to distinguish between them. For instance, PbO is lead *mon*-oxide, PbO_2 is lead *di*-oxide, while Pb_2O_3 is lead *sesqui*-oxide (the atomic ratio 2 : 3 being distinguished by this prefix). This method of forming names is used generally; thus InCl, $InCl_2$, and $InCl_3$ are called indium *mono*-, *di*-, *tri*-chloride respectively, etc.

[2] When two basic oxides of a metal are known, the suffixes *-ous* and *-ic* are employed to distinguish between them, the *-ic* oxide having the greater oxygen content; *e.g.* FeO is *ferrous* oxide and Fe_2O_3 is ferr*ic* oxide.

An oxide which is neither acidic nor basic, but which contains more oxygen than the basic oxides of the metal, is usually called a *peroxide*; *e.g.* barium peroxide, BaO_2, manganese peroxide, MnO_2. Some peroxides—for instance, barium peroxide—are derivatives of hydrogen peroxide, and yield that substance when acted upon by an acid. Others, like manganese peroxide, behave as oxidising agents in the presence of acids. The term *peroxide* is sometimes used in another sense to indicate oxides which contain a larger proportion of oxygen than the typical oxides according to the periodic classification. On this definition manganese dioxide, MnO_2, is not a peroxide, since the typical oxide is Mn_2O_7. Persulphuric anhydride, S_2O_7, however, is a peroxide, since the typical oxide is SO_3.

An oxide which is neither acidic nor basic and does not yield such oxides by loss of oxygen is called a *neutral* oxide. Water, H_2O, and tellurium monoxide, TeO, are examples. *Suboxides*, or oxides containing less oxygen than the lowest basic oxides of the same metals, may also be included among the neutral oxides, *e.g.* lead suboxide, Pb_2O.

Lastly, there are oxides which may be termed *mixed anhydrides*, e.g. chlorine dioxide, ClO_2 or Cl_2O_4, which yield a mixture of acids when they react with water—

$$Cl_2O_4 + H_2O = HClO_3 + HClO_2$$

and *saline oxides*, which are regarded as salts; *e.g.* lead sesquioxide, Pb_2O_3, which is looked upon as lead plumbate, $Pb.PbO_3$.

A number of oxides are both acidic and basic, according to circumstances. Thus aluminium oxide behaves towards hydrochloric acid as a basic oxide, forming a salt (aluminium chloride) and water. Towards sodium hydroxide, however, it behaves as an acidic oxide, forming a substance called sodium aluminate, which must be regarded as a salt formed by a process quite analogous to the production of sodium chromate from sodium hydroxide and chromic anhydride. Oxides exhibiting this double function are called *amphoteric oxides*, and their hydroxides *amphoteric hydroxides* (*vide infra*, p. 227).

Hydroxides, Bases, Alkalis.—The monoxides of the alkali metals combine readily with water, forming solid substances termed alkali *hydroxides*,[1] *e.g.*

$$K_2O + H_2O = 2KOH.$$

The monoxides of the alkaline earth metals also unite readily with water to form hydroxides, *e.g.*

$$CaO + H_2O = Ca(OH)_2.$$

Hydroxides corresponding to the weakly basic oxides such as zinc oxide and aluminium oxide are known. They cannot be prepared directly from an oxide and water, but are obtained readily by double decomposition; *e.g.* zinc hydroxide, $Zn(OH)_2$, is precipitated when potassium hydroxide solution is added to a solution of zinc chloride—

$$ZnCl_2 + 2KOH = Zn(OH)_2 + 2KCl.$$

For reasons which cannot be entered into here, hydroxides are regarded as compounds containing the hydroxyl radicle (OH), a view which accounts for the name and the method employed in writing their formulæ.

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[1] These are often, but quite wrongly, called *hydrates*. See p. 200.

The term *base* is now usually employed in inorganic chemistry to mean *basic hydroxide.* The hydroxides of the alkali metals are also known as *alkalis.* The basic character exhibited by an aqueous solution of ammonia is attributed to the existence in the solution of ammonium hydroxide $(NH_4)OH$, in which the ammonium radicle (NH_4) exhibits the characteristics of an atom of metal.[1]

The normal hydroxide corresponding with the oxide M_xO_y is $M_xO_y.yH_2O$; or, as it is written, $M_x(OH)_{2y}$. The normal hydroxides of most basic oxides are known, and, by careful drying, may often be made to yield hydroxides with a smaller water content. Such hydroxides are sometimes met with as minerals, *e.g.* diaspore, $Al_2O_3.H_2O$. The hydroxides of the acidic oxides constitute the oxyacids, and it is seldom that normal hydroxides, in which hydroxylation is at a maximum, can be realised. For example, the normal hydroxide corresponding to P_2O_5 is $P(OH)_5$, but the most fully hydroxylated hydroxide known is orthophosphoric acid, H_3PO_4, *i.e.* $P(OH)_5 - H_2O$.[2]

Salts.—A salt is a compound derived from an acid by the replacement of the acidic hydrogen by the metal or basic radicle such as (NH_4), (UO_2), etc.; accordingly acids are often described as "salts of hydrogen." A general method of effecting the replacement, by the interaction of an acid with a basic oxide, has already been mentioned.[3] The terms *normal* and *acid* salt have also been explained (p. 196). Substances known as *basic salts* may be looked upon as compounds of normal salts with basic oxides or hydroxides, as salts of basic radicles or as hydroxides in which part of the hydroxyl has been replaced by an acid radicle. Bismuth oxychloride or basic bismuth chloride, for example, may be represented as $BiCl_3.Bi_2O_3$ or $BiO.Cl$, according to the view adopted, and basic lead chloride as $PbCl_2.Pb(OH_2)$ or $Pb(OH)Cl$. There is little doubt that many "basic salts" described in the literature are simply mixtures.

The salts of the hydracids must be carefully distinguished from the compounds of non-metals with the halogens, cyanogen, etc. The latter are not salts; they cannot be formed from basic oxides and the requisite acids, and they exhibit none of the characteristics of the salts of the hydracids. Thus they are decomposed by water (hydrolysed), the change being irreversible, *e.g.*

$$BBr_3 + 3H_2O = B(OH)_3 + 3HBr;$$

they are easily volatile, frequently being liquids at ordinary temperatures, concentrated sulphuric acid does not affect them, and they are readily soluble in such solvents as ether, chloroform, benzene, etc. The halogen compounds of the metalloids approach these compounds in some of their properties; but each metalloid forms at least one oxide possessing basic properties, and consequently yields halogen compounds which may be formed by the ordinary method for obtaining salts, namely, from the basic oxide and acids, even although the salts thus formed are decomposed by water. In short, the reactions between the oxides and acids are reversible.[1]

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[1] See this series, Vol. II.

[2] The name *ortho*-acid is applied in [illegible] the most fully hydroxylated acid known that corresponds to a particular anhydride. An acid, the molecule of which may be regarded as derived from the molecule of an ortho-acid by the loss of a whole number of molecules of water is called a *meta*-acid; *e.g.* HPO_3, *i.e.* $(H_3PO_4 - H_2O)$, is termed metaphosphoric acid. The term *pyro*-acid denotes an acid, the molecule of which is regarded as derived in a similar fashion from two molecules of ortho-acid; *e.g.* $H_4P_2O_7$, *i.e.* $(2H_3PO_4 - H_2O)$, is called pyrophosphoric acid.

[3] A salt is said to *correspond to* or to be *derived from* the basic oxide from which it may be thus obtained; and the terminations *-ous* and *-ic* which are applied to the names of the basic oxides are also used in naming salts. Thus the chloride corresponding to ferr*ous* oxide is called ferr*ous* chloride, that derived from ferr*ic* oxide is called ferr*ic* chloride, etc.

Hydrates.—Many acids, bases, and salts enter into combination with water, forming crystalline solid substances known as hydrates, the compositions of which are in conformity with the ordinary laws of chemical combination. For example, when zinc sulphate is obtained from an aqueous solution at the ordinary temperature, by evaporation of the solvent, it separates as the heptahydrate $ZnSO_4.7H_2O$. In general, the composition of a hydrate is such that it may be represented as x molecules of acid, base or salt, associated with y molecules of water. Hydrates often lose water very readily when heated, leaving behind either the anhydrous substance or a lower hydrate, *i.e.* one containing less water; these changes are reversible. It is customary to speak of hydrates as containing "water of crystallisation," although, since many crystalline substances do not contain any such water, the expression is misleading; the zinc sulphate is said to contain seven molecules of water of crystallisation.[2]

Double Salts and Complex Salts.—Many instances are known of combination between salts, two and sometimes three single salts uniting together in simple molecular ratios to produce a substance which, in the solid state, possesses physical properties quite distinct from those of the single salts. These substances frequently contain water of crystallisation. For example, the substance $3NH_4Cl.ZnCl_2$ can be crystallised out from a solution containing zinc chloride and ammonium chloride, and the substance $FeSO_4.(NH_4)_2SO_4.6H_2O$ from a solution containing ferrous sulphate and ammonium sulphate.

In aqueous solution many of these substances behave in the manner that would be expected of a mere mixture of the constituent simple salts, and they are accordingly called *double* or *triple* salts as the case may be. Examples are known of double salts derived from two different salts of the same acid; *e.g.* $K_2SO_4.Al_2(SO_4)_3.24H_2O$, from two different salts of the same metal; *e.g.* $Hg(NO_3)_2.2HgS$, and from two different salts of two different acids; *e.g.* kainite, $MgSO_4.KCl.3H_2O$. Of these types the first is by far the most frequently observed.

The formation of a double salt from two single salts is a reversible process. When the two salts have a common ion, the systems formed from the double salt, single salts and water are three-component systems. The assemblage of the four phases mentioned constitutes a univariant system, and hence, to any particular pressure there corresponds only one temperature, the *transition-point*, at which equilibrium is possible. For example, at atmospheric pressure, copper calcium acetate decomposes at 75° into the single salts.

$$\begin{aligned}Ca(C_2H_3O_2)_2.Cu(C_2H_3O_2)_2.8H_2O = {} & Ca(C_2H_3O_2)_2.H_2O \\ & + Cu(C_2H_3O_2)_2.H_2O + 6H_2O.\end{aligned}$$

Above 75° the double salt does not permanently exist, but breaks up into the single salts; the reverse holds below that temperature. It will be noticed that the water of crystallisation of the double salt is greater than that of the single salts. The reverse is the case with astracanite, $MgSO_4.Na_2SO_4.4H_2O$, formed in accordance with the equation

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[1] The non-metals are further distinguished from metals by the property of forming volatile hydrides; the few metallic hydrides known are not volatile.

[2] For the application of the Phase Rule to the study of hydrates the reader is referred to the works cited on p. 177.

$$MgSO_4.7H_2O + Na_2SO_4.10H_2O = MgSO_4.Na_2SO_4.4H_2O + 13H_2O,$$

and consequently the double salt is stable above the transition-point, in this case 22°, and not below it.

The thermal changes accompanying such transitions are due mainly to hydration or dehydration, and these processes are attended with evolution and absorption of heat respectively. It is therefore not difficult to see that the directions of the changes in the examples given are in accordance with Le Chatelier's Theorem.[1]

In distinction to the double salts properly so called, there exist substances which may be formulated as double salts and which can usually be produced by the union of two single salts, but which in aqueous solution differ remarkably from the original salts. The compound $2NaCl.PtCl_4$ is an example. From the properties of chlorides it would be expected that six molecular proportions of silver nitrate would be necessary to react with one of the compound; but only two are required. The precipitate, however, is not silver chloride, but has the formula $2AgCl.PtCl_4$. The "double chloride" must, in fact, be looked upon as the sodium salt $Na_2[PtCl_6]$ of a *complex acid* $H_2[PtCl_6]$, the precipitate obtained with silver nitrate being the corresponding silver salt $Ag_2[PtCl_6]$. The acid radicle of these salts is $[PtCl_6]$.

Examples of *complex salts* are very numerous. The ferrocyanides and cobalticyanides, for example, are salts of the complex acids, $H_4[Fe(CN)_6]$ and $H_3[Co(CN)_6]$, and not merely double cyanides. Accordingly, they do not give the reactions usually associated with iron and cobalt salts respectively (*vide infra*, p. 221).

ELECTROLYSIS.

Introductory. Nomenclature and Faraday's Laws.—The various substances through which an electric current can be passed may be divided into two groups. The passage of electricity through a member of the first group is not accompanied by any chemical change; the metals belong to this group. Members of the second group, however, suffer chemical decomposition when the current is passed through them. Such substances are termed *electrolytes*, and the process of decomposition is called *electrolysis*.

Electrolytes comprise fused salts and solutions of acids, bases, and salts in various solvents.[2] The following brief account[3] of the subject of electrolysis deals only with aqueous solutions, except where the contrary is expressly stated. It should be mentioned that pure water itself can scarcely be called an electrolyte, its conductivity (*vide infra*, p. 227) being exceedingly small.

As a typical example of the process of electrolysis, the decomposition of dilute sulphuric acid may be described. When two platinum plates, connected by wires to the terminals of a battery or other source of the electric current, are immersed in the dilute acid, it is noticed that bubbles of gas appear at the platinum surfaces. The gas liberated at the surface of the plate at the higher potential is found to be oxygen; that evolved at the other plate proves to be hydrogen; and if the current continues to flow for some time and precautions are taken to prevent mixing in the solution, it is found that round the higher potential plate the concentration of sulphuric acid increases, while round the other plate a diminution in concentration occurs.

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[1] For the further discussion of double salts, *vide* the works cited on p. 177, and Miss Freund, *Science Progress*, 1907, 5, 135.

[2] It is a common practice to consider that the term "salt" includes the ideas of "acid" and "base," in which case "electrolyte" and "salt" become synonymous.

[3] The reader is referred to the following works for further information: Lehfeldt, *Electrochemistry* (Longmans & Co., 1904); Leblanc, *Electrochemistry*, translated by Whitney and Brown (Macmillan & Co., 1907); Whetham, *Theory of Solution* (Camb. Univ. Press, 1902).

When a dilute solution of copper sulphate is similarly electrolysed, metallic copper is deposited upon the platinum plate at the lower potential, while oxygen is evolved at the other plate, around which sulphuric acid is formed. Ultimately, all the copper becomes deposited, and a dilute solution of sulphuric acid remains which yields hydrogen and oxygen as previously described.

Each of the preceding arrangements constitutes an *electrolytic cell.* The plates which serve to convey the current into and out of the liquid are termed *electrodes*; the one at the higher potential, *i.e.* that by which current enters, is called the *anode*, the other being known as the *cathode.* These terms are due to Faraday,[1] who was the first to make an exhaustive study of this subject. Faraday's idea of the mechanism of electrolysis did not differ greatly from that proposed in 1806 by Grotthus; the substance undergoing decomposition was supposed to be divided into two parts, which travelled in opposite directions towards the electrodes. The "bodies that go to the electrodes" Faraday called *ions*; the *cation* travels to the cathode, the *anion* to the anode.

Davy showed that there is no accumulation of electricity in any part of a voltaic circuit, but that a uniform flow exists throughout. The quantitative laws of electrochemical decomposition were discovered by Faraday[2] and are as follows: (i.) *the amount of decomposition of a given electrolyte is proportional to the quantity of electricity which flows through it, and* (ii.) *the quantities of different substances liberated by the same quantity of electricity are in the ratios of their chemical equivalents.*

The *electrochemical equivalent* of a substance is defined as the mass of the substance liberated by one coulomb of electricity (one ampère flowing for one second). **Faraday's Laws** may therefore be re-stated thus: the amount of a substance liberated is equal to the product of its electrochemical equivalent and the number of coulombs passed, and the electrochemical equivalents of substances are proportional to their chemical equivalents.

Careful experiments have shown that Faraday's Laws are exact. For example, the chemical equivalent of silver is 107·88, and that of copper[3] is 31·790; their ratio is 1 : 0·29468. The electro-chemical equivalents are in the ratio of 1·1175 to 0·32929,[4] *i.e.* of 1 to 0·29467. The laws, moreover, apply to the electrolysis of fused salts;[1] and Richards and Stull found no difference between the electrochemical equivalents of silver when deposited (i.) from an aqueous solution of the nitrate, and (ii.) from a solution of the nitrate in a mixture of fused sodium and potassium nitrates.[2] Solvents other than water have also been employed, *e.g.* pyridine and acetone, and the electrochemical equivalents found to be identical with those obtained when water is the solvent.[3]

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[1] Faraday, *Experimental Researches in Electricity*, 1839, vol. i. p. 195.

[2] Faraday, *opus cit.*, vol. i., Seventh Series of Researches.

[3] Mean of results from (i.) composition of cupric bromide; (ii.) composition of cupric oxide; and (iii.) replacement of silver in silver nitrate by copper, Richards, *Proc. Amer. Acad.*, 1891, **26**, 240; Clarke, *A Recalculation of the Atomic Weights* (Smithsonian Collections), 3rd edition, 1910.

[4] Richards and Heimrod, *Proc. Amer. Acad.*, 1902, **37**, 415. See also Gallo (*Gazzetta*, 1906, **36**, ii. 116); Kreider (*Amer. J. Sci.*, 1905, [iv.], **20**, 1); Washburn and Bates (*J. Amer. Chem. Soc.*, 1912, **34**, 1341, 1515); and Bates and Vinal (*ibid.*, 1914, **36**, 916), on the ratio of the electrochemical equivalents of iodine and silver.

From the many careful determinations of the electrochemical equivalent of silver that have been made,[4] it appears that the value cannot differ appreciably from 1·118 mgms. per coulomb. Hence, the gram-equivalent of silver is liberated by the passage of 107·88/0·001118 = 96,500 coulombs; and by Faraday's Law this quantity of electricity, known as a "faraday," will liberate the gram-equivalent of any other substance that the current is capable of separating.

The nature of the products obtained by electrolytic decomposition leaves little doubt as to what the ions must be. In the case of a salt solution, the cation is a metal, and the anion an acid radicle, *e.g.* the ions of copper sulphate are copper and the sulphate radicle (SO_4). The cation of an ammonium salt is the ammonium radicle (NH_4); that of all acids is hydrogen, the anions being acid radicles. In the case of bases the cations are metals, while the anion is the hydroxyl radicle (OH); *e.g.* the ions of sodium hydroxide are sodium and hydroxyl.

The ability to function as cations is characteristic of metals; the non-metals form anions, either as such, or in combination with other non-metals, forming a compound ion or acid radicle. A metal may, however, form part of an anion, *e.g.* the anion of potassium permanganate is the MnO_4 radicle; further, the cation of ammonium salts is an example of a cation composed of non-metals.

To account for the quantitative phenomena of electrolysis it is necessary to suppose that the motion of the ions through the electrolyte is associated with the motion of electricity. The gram-equivalent of each ion is regarded as conveying one faraday of electricity to the electrode towards which it moves. In accordance with the laws of electrostatics, cations must carry a positive, and anions a negative charge; whence the metals and non-metals are known as *electropositive* and *electronegative* elements respectively. When the ions reach the electrodes, they give up their electric charges; what happens subsequently depends upon the chemical nature of the ions, the electrodes, and the solvent. The ion, deprived of its charge, may be liberated in the free state, *e.g.* hydrogen and copper at the cathode in the examples the uni-univalent, uni-bivalent, and bi-bivalent salts respectively.[1] With substances, such as ammonia, which in aqueous solution have very small equivalent conductivities the influence of concentration is enormous, and the data, even for very dilute solutions, do not indicate that a limiting value is being approached; from indirect evidence, however, this is assumed to be the case.

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[1] Lorenz, *Zeitsch. Elektrochem.*, 1900, **7**, 277; 1901, **8**, 753; Richards and Stull, *Proc. Amer. Acad.*, 1902, **38**, 409.

[2] It has also been shown that the electrochemical equivalent of silver is independent of the pressure from 1 to 1500 atmospheres (Cohen, *Zeitsch. Elektrochem.*, 1913, **19**, 132).

[3] Kahlenberg, *J. Physical Chem.*, 1900, **4**, 349; Skinner, *Brit. Assoc. Report*, 1901.

[4] Rayleigh and Sidgwick, *Phil. Trans.*, 1884, **175**, 411; F. and W. Kohlrausch, *Wied. Annalen*, 1886, **27**, 1; Patterson and Guthe, *Phys. Review*, 1898, **7**, 257; Kahle, *Wied. Annalen*, 1899, **67**, 1; Richards, Collins, and Heimrod, *Proc. Amer. Acad.*, 1899, **35**, 123; Richards and Heimrod, *ibid.*, 1902, **37**, 415; Richards, *ibid.*, 1908, **44**, 91; Guthe, *Phys. Review*, 1904, **19**, 138; Van Dijk and Kunst, *Ann. Physik*, 1904, **14**, 569; Van Dijk, *ibid.*, 1906, **19**, 249; Smith, Mather, and Lowry, *Phil. Trans.*, 1908, **A**, **207**, 545; Laporte and de la Gorce, *Bull. Soc. internat. Electriciens*, 1910, **10**, ii. 157; Jaeger and von Steinwehr, *Zeitsch. Instrumentenkunde*, 1908, **28**, 327, 353; Rosa, Vinal, and M'Daniel, *Bull. U.S. Bureau of Standards*, 1911, **8**, 367; Duschak and Hulett, *Trans. Amer. Electrochem. Soc.*, 1907, **12**, 257; Foerster and Eisenreich, *Zeitsch. physikal. Chem.*, 1911, **76**, 643.

Kohlrausch observed that the limiting values λ_∞ of the equivalent conductivities of electrolytes could be represented in each case as the sum of two independent quantities, one depending solely on the anion, the other on the cation; these parts are called *ionic conductivities*. The values for a number of ions are given in the accompanying table; the differences between the two series of values for 18° and 25° give an idea of the rate at which the conductivity of an electrolyte changes with temperature.[2]

TABLE OF IONIC CONDUCTIVITIES.

Ion.	18°.	25°.	Ion.	18°.	25°.	Ion.	18°.	25°.
$Cs^{\cdot}$	68·0	...	$H^{\cdot}$	314·5	350·0	I'	66·6	76·5
$Tl^{\cdot}$	65·9	76·0	$Pb^{\cdot\cdot}$	60·8	71·0	Cl'	65·5	75·8
$NH_4^{\cdot}$	64·7	..	$Ba^{\cdot\cdot}$	55·4	65·2	NO_3'	61·8	70·6
$K^{\cdot}$	64·5	74·8	$Ca^{\cdot\cdot}$	51·9	60·0	BrO_3'	47·6	51·8
$Ag^{\cdot}$	54·0	63·4	$Mg^{\cdot\cdot}$	45·9	55·0	SO_4''	68·5	80·0
$Na^{\cdot}$	43·4	51·2	$Cu^{\cdot\cdot}$	45·9	.	$Fe(CN)_6''''$	95·0	110·5

The preceding regularity, known as *Kohlrausch's Law*, is assumed to hold good in all cases. On this assumption it is easy to deduce indirectly the values of λ_∞ for such substances as ammonium hydroxide; *e.g.* in the case mentioned, the required limiting value is the sum of the ionic conductivities of the ammonium and hydroxyl ions, and these can be obtained from data supplied by other salts for which λ_∞ may be directly determined.

Migration of Ions; Transport Numbers.—In accordance with the view already explained, electrolysis is considered as a process resembling convection, a constant stream of cations moving with the current and carrying positive electricity to the cathode, and a stream of anions conveying negative electricity in the opposite direction. In the interior of an electrolyte, therefore, the total current is the sum of two currents which may be termed the cationic and anionic currents respectively. Although the cations and anions are discharged at the electrodes in the ratios of their chemical equivalents, it does not necessarily follow that the cationic and anionic currents are equal; their relative magnitudes depend upon the speeds of the cations and anions, which in general are not equal.

The relative speeds of the ions in a given solution may be determined by passing a measured quantity of electricity through the solution and estimating the changes in concentration in the portions of the solution immediately surrounding the electrodes. The first measurements of this kind were made by Hittorf,[1] who correctly interpreted them as indicating that the ions moved with different speeds. For details of the experimental methods, which have to be adapted to suit particular cases, reference must be made to other works.[2] The relative speeds of the anion and cation are proportional to the changes of concentration around the cathode and anode respectively, provided that care is taken to prevent mechanical mixing, and that the experiment is not prolonged for a sufficient length of time to lead to a change of concentration in the middle portion of the solution.

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[1] A *uni-univalent* salt yields two univalent ions, *e.g.* NaCl yields $Na^{\cdot}$ and Cl'; a *uni-bivalent* salt yields two univalent ions and a bivalent ion, *e.g.* Na_2SO_4 yields 2 $Na^{\cdot}$ and SO_4'', and $BaCl_2$ yields $Ba^{\cdot\cdot}$ and 2 Cl'; a *bi-bivalent* salt yields two bivalent ions, *e.g.* $CuSO_4$ yields $Cu^{\cdot\cdot}$ and SO_4'', etc.

[2] For values at temperatures between 0° C. and 156° C. see Johnston, *J. Amer. Chem. Soc.*, 1909, **31**, 1010.

The results of migration experiments are expressed by means of *transport* or *transference numbers*. For the ions of a given electrolyte these numbers are such that (i.) they are proportional to the relative speeds of the ions, and (ii.) their sum is unity. They therefore represent the cationic and anionic currents as fractions of the total current. The transport numbers for the ions of a uni univalent electrolyte are, in dilute solutions, practically independent of the concentration, and the same is true for uni bivalent electrolytes, with the exception of the halides and sulphates of the bivalent metals, for which the cation transport number steadily increases with the dilution. With rise of temperature, transport numbers above 0·5 decrease, and those below 0·5 increase, so that the difference between the speeds of the ions of an electrolyte diminishes with rise of temperature.[3]

As has been remarked already, since an electrolyte obeys Ohm's Law, it follows that the speed of an ion is proportional to the potential gradient The speeds U and V of the cation and anion under unit potential gradient (one volt per cm.) are called the *mobilities* of the ions, and, on the convective view of electrolysis, it may be shown that

$$\kappa = 96{,}500\eta(\mathrm{U} + \mathrm{V}),$$

in which κ and η are measured in the units already stated, and U and V in cms. per second. Now, the transport numbers are proportional to U and V; hence, by combining them with measurements of κ and η, it is possible to calculate the mobilities of the ions.

The ionic mobilities thus deduced are very small, amounting to only a few centimetres per hour, and they are found to increase with the dilution, approaching, however, towards limiting values. This will be at once evident from what has been stated already concerning the variation of κ/η, the equivalent conductivity, with the dilution. Moreover, the limiting value for the ionic mobility of, say, the chlorine ion, is found to be the same for all electrolytes in which chlorine is the anion, *i.e.* it is independent of the nature of the cation. This is only another way of expressing Kohlrausch's Law, which is thus seen to be in accordance with the convective view of electrolysis, provided that the ions are supposed to possess complete migratory independence.

The preceding equation, for extremely dilute solution, becomes

$$\lambda_{\infty} = \left(\frac{\kappa}{\eta}\right)_{\eta=0} = 96{,}500(\mathrm{U}_{\infty} + \mathrm{V}_{\infty}).$$

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[1] Hittorf, *Pogg. Annalen*, 1853, 89, 177; 1856, 98, 1; 1858, 103, 1, 1859, 106, 337, 513; Ostwald's *Klassiker*, Nos. 21 and 23.

[2] *E.g.* the works mentioned on pp. 201 and 204.

[3] For a collection of the available data on transport numbers, and a critical discussion of the same, *vide* Noyes and Falk, *J. Amer. Chem. Soc.*, 1911, 33, 1436.

Kohlrausch's ionic conductivities are therefore 96,500 U_∞ and 96,500 V_∞. In order to express the conductivity of a solution of finite concentration in terms of U_∞ and V_∞, the equation must be written

$$\kappa = 96{,}500\eta\gamma(U_\infty + V_\infty),$$

in which γ is a proper fraction, which varies with η; its significance will be discussed later.

It remains to be mentioned that ionic mobilities have been measured directly by various experimenters, with results in good agreement with those calculated by the method outlined above; owing to lack of space, however, the reader must be referred to other works or the original memoirs for details of the methods.[1]

THE THEORY OF DILUTE SOLUTIONS.

In 1885 Van't Hoff[2] pointed out that a remarkable analogy existed between dilute solutions exerting osmotic pressure (p. 124) on the one hand, and gases under ordinary pressures on the other. He arrived at his results by thermodynamic reasoning, the conception of a semi-permeable membrane (p. 123) rendering it easy to apply the second law of thermodynamics to the investigation of the properties of solutions.

In the case of a *dilute* solution of a *perfect* gas in a solvent, the solubility conforming to *Henry's Law* (p. 101), the following remarkable result was deduced:—

The osmotic pressure exerted by the substance in solution is equal to the pressure that the substance would exert if it existed in the gaseous state at the temperature of the solution and occupied a volume equal to that of the solution.

Accordingly, at constant temperature the osmotic pressure of the solution is proportional to the concentration; at constant concentration the osmotic pressure is proportional to the absolute temperature; and, if P, T, and V denote the osmotic pressure, absolute temperature and volume of solution containing one gram-molecule of solute, then

$$PV = RT,$$

where R is the ordinary gas constant (p. 27).

Van't Hoff's deduction amounts to an extension of Avogadro's Hypothesis to dilute solutions, and may be put in the form that equal volumes of all dilute solutions which, at the same temperature, exert equal osmotic pressures, contain equal numbers of molecules of solute; this number, moreover, being the same as the number of molecules contained in an equal volume of a perfect gas at the same temperature and under a pressure equal to that of the osmotic pressure of the solutions.

The preceding generalisation, theoretically deduced for dilute solutions of perfect gases, was *assumed* by Van't Hoff to hold good for *dilute solutions of all solutes*. Pfeffer's measurements of osmotic pressures (p. 124) supplied valuable confirmation of this assumption, but were not very numerous.

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[1] *Vide* the works cited on p. 204, and Whetham, *Phil. Trans.*, 1893, A, **184**, 337; 1895, A, **186**, 507; Masson, *ibid.*, 1899, A, **192**, 331; Steele, *ibid.*, 1902, A, **198**, 105; *cf.* Lewis, *J. Amer. Chem. Soc.*, 1910, **32**, 862.

[2] Van't Hoff, *K. Svenska. Vet.-Akad. Handl.*, 1885, **21**, 38; *Zeitsch. physikal. Chem.*, 1887, **1**, 481; *Phil. Mag.*, 1888, [v.], **26**, 81.

By means of the laws of thermodynamics it is possible to connect the osmotic pressure of a solution with its vapour pressure[1] and freezing-point; hence the accuracy of Van't Hoff's views may be tested from measurements of vapour pressures and freezing-points, which are much less difficult to determine experimentally. This course was adopted by Van't Hoff, who showed that if his theory were correct, then all the laws relating to the lowering of the vapour pressure (p. 114) followed as a necessary consequence. Moreover, he proved that Raoult's "molecular depression of the freezing-point" of a solvent[2] should be equal to $0{\cdot}02T^2/L$, T being the absolute temperature of freezing, and L the latent heat of fusion of the solvent in calories. The following results supplied the experimental confirmation of this deduction:—

Solvent.	T.	L.	$\frac{\cdot 02T^2}{L}$.	Raoult's Molecular Depression.
Water	273·0	79	18·9	18·5
Acetic acid	289 7	43·2	38 8	38 6
Formic acid	281·5	55·6	28 4	27·7
Benzene	277 9	29·1	53	50
Nitrobenzene	278·3	22·3	69 5	70·7
Ethylene dibromide . . .	280·9	12·94	122	117·9

Van't Hoff's theory is therefore seen to hold good for dilute solutions, and Raoult's Laws receive a theoretical interpretation.[3]

It is desirable to explain more fully what the term "dilute" really signifies. A dilute solution, to which Van't Hoff's theory is strictly applicable, must be such that its volume does not differ appreciably from the volume of the solvent contained in it, and the heat of dilution must be nil. In many solutions to which the term "dilute" is usually applied, *e.g.* tenth-normal solutions, these conditions are by no means fulfilled; in particular, the heat of dilution is frequently appreciable, and molecular weight determinations made with such solutions may therefore be considerably in error when deduced by the usual formulæ given in Chap. IV.[4]

A complete theory that will include concentrated as well as dilute solutions within its scope still remains to be formulated. Attempts towards the solution of this problem have, however, been made by introducing the conception of an "ideal solution." The general characteristics of such a solution are: (i.) the number of different kinds of molecules present is equal to the number of constituents of the solution; (ii.) the physical properties of the solution are connected with the physical properties of its constituents in the pure state by the equation—

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[1] For the exact connection, see Berkeley and Hartley, *Proc. Roy. Soc.*, 1906, **A**, **77**, 156; *Phil. Trans.*, 1906, **A**, **206**, 481; 1908, **A**, **209**, 177; Spens, *Proc. Roy. Soc.*, 1906, **A**, **77**, 234; Porter, *Proc. Roy. Soc.*, 1907, **A**, **79**, 519; 1908, **A**, **80**, 457; Callendar, *Proc. Roy. Soc.*, 1908, **A**, **80**, 466.

[2] The depression produced by one gram-molecule of solute in one hundred grams of solvent, see p. 122.

[3] Translations of Van't Hoff's and Raoult's papers will be found in Harper's *Scientific Memoirs*, 1899, No. 4.

[4] For example, the molecular weight of sodium in mercury solution was found by vapour-pressure measurements (Ramsay, *Trans. Chem. Soc.*, 1889, **55**, 533) to be 16 5 in a solution containing 1 gram atom of sodium to 35·8 gram-molecules of mercury; the correction necessary, owing to the fact that the heat of dilution of the solution is far from negligible, is about 6·2 (Bancroft, *J. Physical Chem.*, 1906, **10**, 319), whence the corrected result is 22·7, showing that sodium in dilute solution in mercury is monatomic. The deviation found by Ramsay may be explained on the assumption that the combination occurs between the sodium and mercury.

$$X = xN + x'N' + x''N'' + \ldots$$

in which X is the molecular property in question (*e.g.* molecular volume, molecular refraction, etc.), x (x', x'' . . .) the molecular property of a constituent in the pure state, and N (N′, N″. . .) its mol fraction;[1] and (iii) the partial vapour pressure p of a constituent having a mol fraction N is given by

$$p = p_0N,$$

p_0 being the vapour pressure of the pure substance in the liquid state at the same temperature. Quite a number of solutions are known, the physical properties of which, over a considerable range of concentration, agree well with those deduced from the conception of an ideal solution.[2]

An "ideal" solution, to which the preceding characteristics apply, must be an extremely simple kind of solution, in which solvent and solute mix without change of volume or liberation of heat to produce a solution in which the components are present in their normal molecular state, association, dissociation, or combination not having occurred. The extent, then, to which the properties of a solution deviate from those of the "ideal" solution may be expected to throw considerable light on the nature of the processes operative in solution; and from this point of view strong evidence has already been forthcoming of combination between solute and solvent in numerous instances with the production of "hydrates" or "solvates" in solution.[3]

Returning to the consideration of dilute solutions, it should be noted that the solutes with which Raoult worked were mainly organic substances, as also were his solvents. Occasionally a solute was met with which exhibited a "molecular depression" only about one half the normal value. A simple explanation of this is to assume that the molecules of the solute are largely associated in pairs in the solution, and that each "complex" produces the effect of a single molecule. With aqueous solutions, although a large number of solutes exhibited the molecular depression 18·5, even more gave a depression of about twice this figure. At first sight it would seem that the higher figure was the normal depression and that the solutes, mainly organic substances, giving a depression of 18·5, are abnormal, being "associated" in aqueous solution; but the value 18·5 is the normal figure calculated from Van't Hoff's equation, and it is therefore the higher figure that needs an explanation. As has been already mentioned, this was supplied by Arrhenius[4] shortly after the publication of Van't Hoff's theory. He pointed out that the abnormal solutes are mainly salts, inorganic acids and bases, aqueous solutions of which, in contradistinction to the solutions of normal substances, are conductors of electricity; and he suggested that in aqueous solution the molecules of acids, bases, and salts are largely "dissociated." The Theory of Electrolytic Dissociation, proposed by Arrhenius, will now be discussed.

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[1] The mol fraction of a constituent is equal to $1/n$th of the number of molecules of the constituent present in n molecules of the solution.

[2] See van Laar, *Zeitsch. physikal. Chem.*, 1894, **15**, 457; Lewis, *J. Amer. Chem. Soc.*, 1908, **30**, 668; Washburn, *ibid.*, 1910, **32**, 653.

[3] See *e.g.* Washburn, *Technology Quarterly*, 1908, **21**, 360, or *Jahrb Radioaktiv. Elektronik*, 1908, **5**, 501; Callendar, *Proc. Roy. Soc.*, 1908, **A**, **80**, 466; *Zeitsch. physikal. Chem.*, 1908, **63**, 641; and also the section on hydration that occurs later in this chapter.

[4] Arrhenius, *Zeitsch. physikal. Chem.*, 1887, **1**, 631.

THE THEORY OF ELECTROLYTIC DISSOCIATION.

Introductory.—From the fact that (with non polarisable electrodes) Ohm's Law holds good in the case of electrolytes whatever the magnitude of the electromotive force applied, a very important result follows: in the interior of an electrolyte, no measurable amount of chemical work can be accomplished by the current. The generally accepted explanation, first advanced by Clausius,[1] is that the function of the current is merely directive, controlling the directions of motion of ions which are already present in the solution in a state of migratory freedom.

The products of electrolysis appear simultaneously at the electrodes as soon as the current flows, no matter how far apart the electrodes may be. From the very low values of the ionic mobilities, therefore, it follows that the first ions discharged cannot have been in combination with one another at the moment preceding the passage of the current. The early hypothesis due to Grotthus[2] regarded the current as actually decomposing into ions the molecules of solute in the immediate vicinity of the electrodes, the intermediate molecules then exchanging partners; the following scheme sufficiently illustrates the idea:—

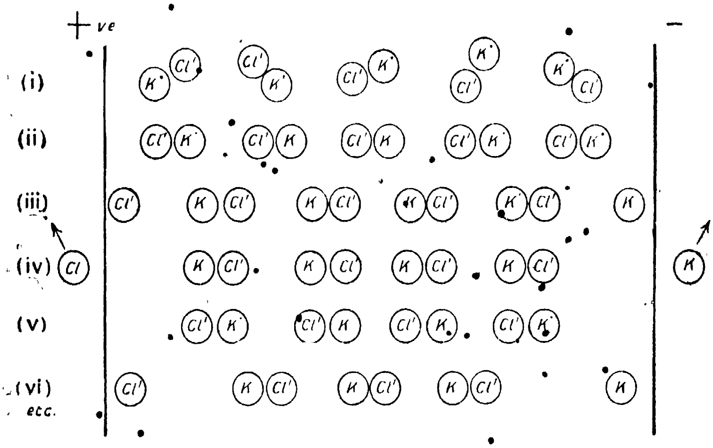

FIG. 72.—(i) Before current; (ii), (iii), (iv), (v) occur successively when current flows, and this process is continuously repeated.

Faraday, however, disproved this idea by showing that the electric forces were the same everywhere between the poles.

Clausius pointed out that on the hypothesis of Grotthus it should not be possible to pass a current through an electrolyte until the electromotive force applied exceeded a certain finite value—a conclusion that is not in harmony with experiment. He supposed that the molecules of solute are always moving about in the solution in a most irregular manner, being driven first one way and then another by collisions with other molecules. As the result of collisions between molecules moving with speeds in excess of the average, some of these molecules get broken up into part molecules carrying electric charges, *i.e.* into what have already been termed ions. Collisions between oppositely charged ions lead to the re-formation of a certain number of molecules, but this is compensated for by the further breakdown of other molecules, so that a certain amount of the solute in a conducting solution is to be regarded as existing in the form of ions. When an electric current is passed through the solution, it simply causes the cations and anions already present to drift in opposite directions towards the electrodes; the undissociated molecules by their impacts supply more ions, which in turn travel to the electrodes, and so on. This theory is purely qualitative, giving no idea of the extent to which dissociation occurs, and the assumption of quite a small degree of dissociation is sufficient to account for the fact that Ohm's Law holds for conducting solutions.

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[1] Clausius, *Pogg. Annalen*, 1857, 101, 338.

[2] Grotthus, *Ann. Chim.*, 1806, 58, 54.

The ideas of Clausius were developed into a quantitative theory by Arrhenius,[1] whose theory of electrolytic dissociation is now generally accepted, at any rate as a valuable working hypothesis. Arrhenius supposed that the molecules of acids, bases, and salts are, as a rule, largely dissociated into their ions in dilute solutions. For instance, a solution of sodium chloride will contain a certain percentage of solute as ordinary molecules, but the remainder (and larger proportion) of the solute will be split up into the ions $Na^{\cdot}$ and Cl'. The undissociated molecules take no part in conveying the electric current, the current being, in fact, due simply to the motion of the electric charges associated with the ions.

On these assumptions it is possible to arrive at a measure of the degree of dissociation of a substance in solution from conductivity measurements. Imagine two large, rectangular, parallel plates to serve as electrodes, placed 1 cm. apart, and suppose 1 c.c of an electrolyte containing 1 gram-equivalent of solute in v c.c. of solution to be placed between the plates, the column of electrolyte having a uniform cross-section. The conductivity of this solution will be K, the specific conductivity. If, however, the entire v c.c. be placed between the plates, the conductivity measured is equal to vK or K/η, *i.e.* to the equivalent conductivity of the solution. With a potential difference of 1 volt between the plates, the conductivity will be numerically equal to the current; and this, according to the views of Arrhenius, will be proportional to the number of ions supplied by the gram-molecule of solute, and to the mobilities of the ions. The latter, of course, depend on the resistance offered to the passage of the ions through the solution, *i.e.* they depend on the viscosity of the solution. Now, the viscosity of a dilute solution only differs from that of the solvent at the same temperature by 1 or 2 per cent., and hence the mobilities of the ions may, in dilute solutions, be regarded as practically independent of the concentration. The important conclusion is therefore reached that the variation of the equivalent conductivity λ of a solution with the concentration is due almost entirely to a change in the number of ions furnished by 1 gram-equivalent of the solute. Accordingly, since λ increases as the concentration diminishes, the degree of dissociation of an electrolyte must increase with the dilution, until, in extremely dilute solutions, the dissociation is complete.

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[1] Arrhenius, *Zeitsch. physikal. Chem.*, 1887, 1, 631; Harper's *Scientific Memoirs*, 1899, No. 4; an interesting account of the development of the theory is given by Arrhenius himself in *J. Amer. Chem. Soc.*, 1912, 34, 353, and in his Faraday Lecture to the Chemical Society (*Trans. Chem. Soc.*, 1914, 105, 1414).

The preceding considerations concerning ionic mobilities justify the method (adopted on p. 208) of expressing the equivalent conductivity of a dilute solution in terms of the ionic mobilities at infinite dilution, by the equation—

$$\lambda = \frac{\kappa}{\eta} = 96{,}500\gamma(U_\infty + V_\infty);$$

and since $$\lambda_\infty = \left(\frac{\kappa}{\eta}\right)_{\eta=0} = 96{,}500(U_\infty + V_\infty),$$

it follows that $$\lambda = \gamma\lambda_\infty.$$

Now λ and λ_∞ have been shown to be proportional to the numbers of ions furnished by the gram-equivalent of solute in the respective solutions, and since λ_∞ refers to a solution in which dissociation is complete, it is clear that γ must represent the fraction of the solute dissociated in the solution of equivalent conductivity λ; in other words, γ is the *degree of dissociation* of the solute. Hence the percentage amount of the solute dissociated into its ions in a dilute solution of equivalent conductivity λ is equal to 100 γ, where

$$\gamma = \frac{\lambda}{\lambda_\infty}.$$

This relationship was deduced by Arrhenius.[1]

Degree of Dissociation of Salts.—The degree of dissociation of electrolytes, as determined by conductivity measurements, may now be briefly discussed, the values at the ordinary temperature (18° C.) being dealt with first.

So far as salts are concerned, a general rule may be stated; with few exceptions, salts of the same ionic type[2] are dissociated to very nearly the same degree in solutions of equal concentrations.[3] Accordingly, it is only necessary to quote the results for a few typical salts; this is done in the following table (*cf.* the values of γ given on p. 205):—

PERCENTAGE DISSOCIATION OF SALTS AT 18° C.[4]

Normality of Solution.	Sodium Chloride.	Lithium Iodate.	Calcium Nitrate.	Potassium Sulphate.	Lanthanum Nitrate.	Copper Sulphate.	Lanthanum Sulphate.
0·001	97·7	97·0	95·4	95·4	...	86·2	...
0·002	96·9	95·8	93·7	93·7	90·2	80·4	46·4
0·01	93·6	91·2	87·6	87·2	80·2	62·9	28·9
0·05	88·2	83·4	78·1	77·1	70·1	45·5	19·8
0·1	85·2	78·9	73·1	72·2	...	39·6	...
0·2	81·8	74·0	67·9	67·3	...	35·1	...
0·5	77·3	68·2	60·9	61·8	...		...
1·0	74·1	64·3	54·9	59·2	...	30·9	...

A normal solution contains 1 gram-equivalent of solute per litre

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[1] For a correction to allow for change of viscosity with change of concentration, see Washburn, *J. Amer. Chem. Soc.*, 1911, **33**, 1461; Green, *Trans. Chem. Soc.*, 1908, **93**, 2049.

[2] *Cf.* footnote on p. 206.

[3] The latter being measured in gram-equivalents per unit volume.

[4] Taken from the collection of data given by Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 454.

The halide salts of the alkali metals all give values very close to those quoted for sodium chloride, whilst the nitrates, chlorates, bromates, and iodates are dissociated to very nearly the same extent as lithium iodate (rather greater, as a rule). The figures for calcium nitrate are typical of those of the uni-bivalent salts of bivalent metals, with the exception of a number of mercury and cadmium salts, for which the dissociation is abnormally small; the values for potassium sulphate are characteristic of those given by uni-bivalent salts of dibasic acids. It will be noticed, by comparing salts at the same (equivalent) dilution, that the degrees of dissociation of salts yielding a univalent ion decrease as the valency of the other ion increases; but that even a uni-tervalent salt is more largely dissociated than a bi-bivalent salt, which, in its turn is dissociated more than a bi-tervalent salt. The degree of dissociation of acids and bases will be discussed later (p. 219).

The variation of the degree of dissociation of an electrolyte with the temperature has been investigated by Noyes and others for a considerable number of substances, at temperatures between 0° and 306° C.[1] In general, the degree of dissociation, at a fixed concentration, slowly decreases with rise of temperature, the rate of decrease increasing as the temperature rises; the values at 0° C. and 18° C. do not differ appreciably.

Degree of Dissociation from Freezing-point Measurements.—It was pointed out by Planck,[2] shortly after Van't Hoff had published his investigations on osmotic pressure, that the abnormally great osmotic pressure and other correlated physical properties of dilute solutions of electrolytes required the hypothesis of some form of electrolytic dissociation. These properties depend upon the number of solute molecules per unit volume of solution, and not upon their nature, and Arrhenius assumed that each ion in solution produced the same osmotic effect as that of an ordinary molecule. Accordingly, in very dilute solutions of electrolytes the molecules of which produce two ions, the "molecular depression" of the freezing-point should be exactly twice the normal value, deduced from measurements with non-electrolytes, or calculated from Van't Hoff's formula; solutes the molecules of which yield three ions, should give three times the normal depression, and so on.

In extremely dilute solutions, accurate determinations of molecular depressions of the freezing-point are very difficult, but, employing the refined method of differential platinum thermometry, Griffiths and Bedford[3] have determined the molecular depressions for a number of electrolytes. The normal value for aqueous solutions, calculated from Van't Hoff's formula, is 18·58° C., and Griffiths actually arrived at this result for solutions of cane sugar between 0·02 and 0·0005 molar. Extremely dilute solutions of potassium chloride gave a molecular depression almost exactly twice this value,[4] and Bedford obtained depressions of twice the normal value with potassium permanganate and magnesium sulphate. Barium chloride and sulphuric acid gave almost exactly three times the normal depression, whilst with potassium ferricyanide four times the normal depression was actually observed." These results are exceedingly interesting and significant, bein exactly what would be expected according to the views of Arrhenius.

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[1] *Cf.* Noyes and others, *Carnegie Institution Publications*, 1907, No. 63; *J. Amer Chem. Soc.*, 1908, **30**, 335; 1909, **31**, 987, 1010; 1911, **33**, 795, 1423.

[2] Planck, *Wied. Annalen*, 1887, **32**, 499.

[3] Bedford, *Proc. Roy. Soc.*, 1910, **A**, **83**, 454.

[4] *I.e.* within the limits of experimental error.

Owing to dissociation being incomplete in ordinary solutions, the molecula depressions will not be exactly twice, thrice, etc., the normal value, but som what less, and from the observed values it is possible, as Arrhenius pointe out, to calculate the degrees of dissociation of the solutes, and thereb institute a comparison between the results obtained in this manner and those deduced from conductivity measurements. If $m+n$ molecules of a solute are dissolved in water, and n molecules dissociate, each yielding k ions, the osmotic pressure will be proportional to $m+nk$ instead of $m+n$. The degree of dissociation γ will be equal to

$$\frac{n}{m+n}.$$

Now the ratio $(m+nk):(m+n)$ is equal to the ratio of the observed molecular depression to the normal value, and is usually denoted by i. Hence

$$i=\frac{m+kn}{m+n}=\frac{m+n}{m+n}+\frac{(k-1)n}{m+n}=1+(k-1)\gamma,$$

or

$$\gamma=\frac{i-1}{k-1}.$$

In order to illustrate the nature of the agreement between values of γ obtained in this way, from freezing-point measurements, and those derived from conductivity measurements, the values of i may be calculated from the values of γ given by the relationship

$$\gamma=\frac{\lambda}{\lambda_\infty},$$

and these values of i compared with those actually measured. This is done for a number of typical salts in the following table:—

COMPARISON OF VALUES OF i DERIVED FROM FREEZING-POINT (f.p.) AND CONDUCTIVITY MEASUREMENTS (c).

Normality.		0·005	0·01.	0·02.	0·05.	0·10.	0·20.	0·50.
KCl	f.p.	1·96	1·94	1·92	1·89	1·86	1·83	1·80
	c.	1·96	1·94	1·92	1·89	1·86	1·83	1·78
$BaCl_2$	f.p.	..	2·76	2·71	2·64	2·58	2·52	...
	c.	..	2·77	2·70	2·60	2·52	2·44	...
$Pb(NO_3)_2$	f.p.	2·78	2·70	2·61	2·45	2·30	2·14	1·85
	c.	2·77	2·69	2·59	2·42	2·27	2·12	1·91
$La(NO_3)_3$	f.p.	...	...	...	3·23	3·12	3·07	...
	c.	...	...	...	3·15	2·99	2·83	...
$K_3Fe(CN)_6$	f.p.	3·68	3·60	3·33	...	...	...	...
	c.	3·61	3·48		...	...	...	...
$MgSO_4$	f.p.	1·69	1·62	1·54	1·42	1·32	1·22	...
	c.	1·74	1·67	1·60	1·51	1·50	1·16	...
$Ca_2Fe(CN)_6$	f.p.	...	...	...	1·51	1·40	1·30	...
	c.	...	...		1·55	1·50	1·47	...

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[1] Adapted from the data compiled by Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 485; also *ibid.*, 1910, **32**, 1011.

It will be seen at once that the two methods do not give identical results, and the differences as a rule are considerably greater than possible differences due to experimental error, particularly with salts which yield polyvalent ions. The general parallelism between the two series of results is, however, unmistakable, and the values clearly increase with the dilution towards the theoretical values for complete dissociation, although the value of *i* for calcium ferrocyanide in 0·05 normal solution is far from the theoretical value 3.

It is beyond the scope of this work to enter fully into the various causes which may possibly be responsible for the discrepancies observed between the two series of values. A short account dealing with *hydration* and *intermediate* and *complex ions* only can be given. It should, however, be mentioned that even with uni-univalent salts for which the agreement is good, the result is almost certainly due to a compensation of errors, the undissociated molecules having an abnormally large, and the ions an abnormally small osmotic effect. Further, the existence in solution of double molecules of a solute such as $Mg_2(SO_4)_2$, for example, would lead to values of *i* by the freezing-point method smaller than would otherwise be the case.

Intermediate and Complex Ions.—Hitherto it has been assumed that the dissociation of salts of the types XCl_2 (XBr_2, $X(NO_3)_2$, etc.), Y_2SO_4, and XSO_4 follow the simple schemes $XCl_2 \rightarrow X^{\cdot\cdot} + 2Cl'$, $Y_2SO_4 \rightarrow 2Y^{\cdot} + SO_4''$, and $XSO_4 \rightarrow X^{\cdot\cdot} + SO_4''$. It is, however, possible that salts of the first two types may dissociate in stages, thus (i.) $XCl_2 \rightarrow XCl^{\cdot} + Cl'$, (ii.) $XCl^{\cdot} \rightarrow X^{\cdot\cdot} + Cl'$; and (i.) $Y_2SO_4 \rightarrow Y^{\cdot} + YSO_4'$, (ii.) $YSO_4' \rightarrow Y^{\cdot} + SO_4''$; and that therefore the *intermediate ions* $XCl^{\cdot}$ and YSO_4' exist in appreciable quantity in moderately dilute solutions. Or it may be that complex molecules of salts of the first and third types, such as X_2Cl_4 and $X_2(SO_4)_2$, exist in the solutions, and dissociate according to the schemes $X_2Cl_4 \rightarrow X^{\cdot\cdot} + XCl_4''$ and $X_2(SO_4)_2 \rightarrow X^{\cdot\cdot} + X(SO_4)_2''$, furnishing *complex ions* XCl_4'' and $X_2(SO_4)_2''$, which dissociate more and more with increasing dilution according to such methods as $XCl_4'' \rightarrow X^{\cdot\cdot} + 4Cl'$ and $X(SO_4)_2'' \rightarrow Y^{\cdot\cdot} + 2\,SO_4''$.

Werner[1] was one of the first to recognise the existence of complex ions and to realise their importance in electrolytic dissociation. His researches and theories will be discussed in Volume IX. in connection with the complex cobaltammines.

It is not difficult to see that if moderately dilute solutions of salts contain appreciable quantities of complex or intermediate ions, the transport numbers of the ions should in all probability vary with the dilution.[2] For a large number of uni-bivalent and bi-bivalent salts the transport numbers of the ions are practically independent of the concentration up to 0·2 normal, which may possibly indicate the absence of intermediate and complex ions to any appreciable extent.[3] The transport numbers of the halides and sulphates of bivalent metals, however, decrease steadily and rapidly with increasing concentration, which may be accounted for by assuming that complex ions, such as $BaCl_4''$ and $Mg(SO_4)_2''$, are formed in considerable quantities at the higher concentrations.

At present it is not possible to determine with accuracy the extent to which intermediate and complex ion formation occurs, and accordingly, fo uni-bivalent salts and those of higher ionic types, a certain amount uncertainty is attached to the meaning of the ratio Λ/λ_{∞}, which has in th preceding pages been regarded as a measure of electrolytic dissociation. It clear that complex ion formation will lead to abnormally low values of *i* b the freezing-point method.

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[1] Werner, *Zeitsch. anorg. Chem.*, 1893, **3**, 294.

[2] The ion $BaCl^{\cdot}$, for instance, would migrate to the cathode, but of the ions $Ba^{\cdot\cdot}$ and Cl', into which it is resolved by dilution, the Cl' travels to the anode.

[3] This conclusion is, however, not necessarily correct; see Noyes and Falk, *J. Amer. Chem. Soc.*, 1911, **33**, 1436; Falk, *ibid.*, 1910, **32**, 1555.

Hydration in Aqueous Solution.—So far the ions of a salt have bee regarded simply as atoms or groups of atoms, carrying electric charges opposite sign and migrating under the influence of a potential gradien quite independently of one another. The considerations upon which thi view has been based do not, however, require the ions to be free from a chemical combination, and there is considerable evidence that in aqueou solution most ions are combined with the solvent to varying degree Probably in many cases the undissociated molecules are also combined wit the solvent, and it is doubtless true that numerous non-electrolytes i aqueous solution are likewise "hydrated,"[1] each molecule combining wit a certain number of molecules of the solvent to form a more or less stabl complex molecule.[2]

Walker and his co-workers[3] concluded that in a number of cases con bination with the solvent is the necessary precursor of electrolytic dissoci tion, although such combination does not necessitate that dissociatio Bousfield and Lowry,[4] however, have gone a step further and regard hydr tion as essential to dissociation, the heat of hydration affording the energ necessary to disrupt the molecule. If such is the case the dissociated solu must be hydrated to a greater extent than the undissociated solute as othe wise there is no force available for producing dissociation.

Only one or two of the reasons brought forward in support of the vie that ions are hydrated can be discussed.[5] Considering, for example, t alkali metals, it is observed that the order of increasing ionic mobilities also the order of increasing atomic weight and atomic volume:—

	Li.	Na.	K.	Rb.	Cs.
Atomic weight . .	6·94	23·00	39·10	85·45	132·81
Ionic mobility at 18° .	33·4	43·4	64·5	67·5	68·0

The reverse would naturally be expected to hold good, the heavier io migrating at a slower rate than the lighter ones, just as in the diffusion these metals into mercury, for which it has been shown[6] that the rates diffusion increase with decreasing atomic weight. An explanation of th anomaly is forthcoming if it be assumed that the ions of the alkali metals are hydrated, the number of molecules of water combined with one charged atom of metal diminishing as the atomic weight increases. It is then possible for the ion of lithium to be heavier than the ion of cæsium, and so account for its lower mobility.[1]

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[1] The terms "solvated" and "solvation" are employed to denote similar ideas wh solvents other than water are considered.

[2] Various attempts have been made to frame general theories of solution from the poi of view of hydration, without having recourse to the ionic theory, but none of these can said to have met with general acceptance. The reader may be referred to Morley a Muir's *Dictionary of Chemistry* (Longmans & Co., 1894, vol. iv.), article on solutio part 2; also to Armstrong, *Chem. News*, 1911, **103**, 97, and *Ann. Report Chem. Soc.*, 190 **4**, 17, 21; 1908, **5**, 21; 1911, **8**, 13; Lowry, *Science Progress*, 1908, **3**, 124.

[3] Walker, M'Intosh and Archibald, *Trans. Chem. Soc.*, 1904, **85**, 1098.

[4] Bousfield and Lowry, *Phil. Trans.*, 1904, **204**, 282; *Trans. Faraday Soc.*, 1905, 197; 1907, **3**, 123.

[5] For a valuable summary of the evidence bearing on the subject of hydration in soluti see Washburn, *Technology Quarterly*, 1908, **21**, 360; or *Jahrb. Radioaktiv. Elektron* 1908, **5**, 504.

[6] von Vogau, *Ann. Physik.*, 1907, [iv.], **23**, 369.

It has been found that ionic conductivities increase with rise of temperature in a manner that corresponds very closely to the change of the fluidity (reciprocal of the viscosity) of water with change of temperature. In fact, for a number of slow-moving ions, the parallelism is almost exact. This is not due to increased dissociation, since this latter is actually retarded to a slight extent by rise of temperature. The increase in conductivity is attributable to greater *ionic mobility* consequent upon a change in the frictional resistance experienced by the ion in its passage through the solution. The remarkable fact that this resistance changes at almost precisely the rate at which the viscosity of water (which measures the frictional resistance that one molecule of water experiences in moving about among the others) changes, led Kohlrausch[2] to believe that an ion is associated with a certain number of molecules of water, this water forming a kind of "atmosphere" about the ion and the "complex" moving as a whole through the solution. The fact that a rise in temperature slightly decreases the extent of dissociation may be explained on the assumption that the heat tends to reduce the hydration of the ions and thus facilitates their union to form undissociated molecules.[3]

If the two ions of a salt are hydrated unequally, the passage of electricity through an aqueous solution of the salt must result in a net transference of water in one direction or the other, according to circumstances. If, then, a small quantity of a non-electrolyte be added to the solution, its concentration should increase around one electrode and decrease around the other. By this device, it has been shown experimentally that the ions of hydrochloric acid,[4] and of the chlorides of the alkali metals,[5] are unequally hydrated.

Hydration, and hence dissociation, may be expected to increase with dilution until a maximum is reached after which further hydration has no effect. The average amount of water in combination need not be a whole number. In all probability it is an indefinite assemblage of aqueous molecules.[6]

Owing to hydration, the calculations explained in the preceding pages must often be inexact, and the errors involved cannot as a rule be determined owing to lack of accurate data concerning the extent of hydration. Hydration of any kind obviously renders the statement of concentration, in terms of parts of solute per part of solvent, inaccurate, since part of the solvent must be reckoned as belonging to the solute. Accordingly, abnormal osmotic pressures, freezing-point depressions, etc., may be due in part to this cause, and the abnormality will be the more pronounced the greater the concentration of the solution.[1] Potassium and cæsium nitrates are exceptions in that they behave like ideal binary electrolytes.[2] Hydration of the ions clearly renders measurements of transport numbers slightly inaccurate. Since, moreover, it is probable that, in certain cases, the degree of hydration of an ion changes with the concentration,[3] a change which would doubtless alter its ionic mobility, the possibility of an error due to this cause in taking λ/λ_{∞} as the measure of the degree of dissociation must be recognised.[4]

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[1] Euler, *Wied. Annalen*, 1897, 63, 273; Bredig, *Zeitsch. physikal. Chem.*, 1894, 13, 277.

[2] Kohlrausch, *Proc. Roy. Soc.*, 1903, 71, 338; *Sitzungsber. preuss. Akad. Wiss.*, 1902, 26, 579.

[3] See H. C. Jones and his co-workers, *Amer. Chem. J.*, 1910, 43, 187; 1911, 46, 240 and 368; A. A. Noyes, Y. Kato and Sosman, *J. Amer. Chem. Soc.*, 1910, 32, 159.

[4] Buchböck, *Zeitsch. physikal. Chem.*, 1906, 55, 563.

[5] Washburn, *Technology Quarterly*, 1908, 21, 287; or *J. Amer. Chem. Soc.*, 1909, 31, 322.

[6] Bousfield, *Phil. Trans.*, 1906, A, 206, 101.

Dissociation of Acids and Bases.—Salts, with few exceptions, are largely dissociated, the extent varying from 40 to 85 per cent. for different salts in tenth-normal solution. Acids and bases exhibit a much greater variation in this respect. The monobasic acids such as nitric, hydrochloric, hydrobromic, hydriodic, perchloric, chloric, bromic, iodic, permanganic, thiocyanic, etc., acids, are extensively dissociated in dilute solution, the values comparing with those for uni-univalent salts; in the case of the first four acids mentioned, the values are even greater. Hydrofluoric acid is much less dissociated, only, in fact, to the extent of 7 per cent. in normal solution. Nitrous, hydrocyanic, and acetic acids (and a host of organic acids) are only dissociated to an exceedingly slight degree (see p. 223).

The polybasic acids are not dissociated to so great an extent as the monobasic acids just mentioned above. The quantitative relations, too, are rendered extremely complicated by the fact that the dissociation of these acids proceeds in stages, and hence a number of different kinds of anions are present in solution. Thus, sulphuric acid, one of the most largely dissociated of the dibasic acids, dissociates in two stages—

$$\text{(i.) } H_2SO_4 \rightleftharpoons H^{\cdot} + HSO_4'$$
$$\text{(ii.) } HSO_4 \rightleftharpoons H^{\cdot} + SO_4''.$$

In very dilute solutions the concentration of SO_4'' exceeds that of HSO_4', but in most concentrated solutions the reverse obtains.[5] Phosphoric acid, H_3PO_4, dissociates in three stages—

$$\text{(i.) } H_3PO_4 \rightleftharpoons H^{\cdot} + H_2PO_4',$$
$$\text{(ii.) } H_2PO_4' \rightleftharpoons H^{\cdot} + HPO_4''$$
$$\text{(iii.) } HPO_4'' \rightleftharpoons H^{\cdot} + PO_4'''.$$

In a solution containing one gram-molecule in ten litres, stage (i.) proceeds to about 28 per cent. Dissociation as represented by (ii.) is slight, and as represented by (iii.) almost negligible. Pyrophosphoric acid $H_4P_2O_7$ dissociates in four stages, of which the first two occur to a considerable, the last one practically to a negligible extent.[6]

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[1] See Jones and his co-workers, *Amer. Chem. J.*, 1904, **31**, 356; 1905, **33**, 534; *Zeitsch. physikal. Chem.*, 1906, **55**, 385. Biltz, *ibid.*, 1902, **40**, 185; 1903, **43**, 41; 1906, **56**, 463. Smits, *ibid.*, 1902, **39**, 385.

[2] Biltz, *loc. cit.*; Jahn, *Zeitsch. physikal. Chem.*, 1900, **33**, 545; 1900, **35**, 1; 1901, **37**, 490; Nernst, *ibid.*, 1901, **38**, 487.

[3] Biltz (*loc. cit.*) and Jones (*Zeitsch. physikal. Chem.*, 1906, **55**, 385) attempted to determine the extent of ionic hydration, and both now agree that it increases with dilution. Bousfield (*ibid.*, 1905, **53**, 257) has arrived at the same conclusion.

[4] Interesting examples of the simultaneous occurrence of complex ion formation and hydration are furnished by the halide salts of copper and cobalt; see Donnan and Bassett, *Trans. Chem. Soc.*, 1902, **81**, 939; Vaillant, *Ann. Chim. Phys.*, 1903, (vii.), **28**, 213; Kohlschutter, *Ber.*, 1904, **37**, 1168; Lewis, *Zeitsch. physikal. Chem.*, 1906, **56**, 223; Denham, *ibid.*, 1909, **65**, 641.

[5] Luther, *Zeitsch. Elektrochem.*, 1907, **13**, 296; Noyes and Eastman, *Carnegie Institution Publications*, 1907, **63**, 274; Noyes and Stewart, *J. Amer. Chem. Soc.*, 1910, **32**, 1133.

[6] Abbot and Bray, *J. Amer. Chem. Soc.*, 1909, **31**, 760.

Carbonic, hydrosulphuric, and boric acids, H_2CO_3, H_2S, and H_3BO_3, respectively, likewise dissociate in stages; but in these particular cases the first stage proceeds to an exceedingly slight degree, and the remaining stages to an even smaller extent (see p. 223).

The very soluble inorganic bases, namely the hydroxides of the alkali metals, are dissociated in aqueous solution to about the same extent as uni-univalent salts; the hydroxides of barium, strontium, and calcium rather less. Ammonium hydroxide, however, is only slightly dissociated, the extent in normal solution being less than 1 per cent. (see p. 223).

Some Applications of the Dissociation Theory.—The neutralisation of hydrochloric acid by sodium hydroxide in dilute aqueous solution, expressed in the ordinary way by the equation—

$$NaOH + HCl = NaCl + H_2O,$$

should, according to the ionic theory, be represented thus—

$$Na^{\cdot} + OH' + H^{\cdot} + Cl' = Na^{\cdot} + Cl' + H_2O,$$

since hydrochloric acid, sodium hydroxide, and sodium chloride are almost completely dissociated, whilst water is only dissociated to a minute extent. The change may therefore be expressed simply as

$$H^{\cdot} + OH' = H_2O.$$

Obviously this expresses the essential character of the change whatever acid or base be chosen, provided that both are largely dissociated in dilute solution. The heats of neutralisation in all such reactions should therefore be equal, and, as has been seen already, this is found to be the case. From the data already given (p. 167) it follows that

$$H^{\cdot} + OH' = H_2O + 13{\cdot}7 \text{ Cals.}$$

When either the acid or the base is only slightly dissociated in dilute solution, the observed heat of neutralisation is practically 13·7 Cals. plus the heat of ionisation of the acid (or base, as the case may be); that is to say, the sum of the heat tones of the reactions

$$\text{(i.)} \quad HA = H^{\cdot} + A', \text{ and}$$
$$\text{(ii.)} \quad H^{\cdot} + OH' = H_2O.$$

The heat of neutralisation may therefore be greater or less than 13·7 Cals., since in some cases (i.) is exothermic and in others endothermic.

The Law of Thermo-neutrality (p. 167) is readily explained. Supposing, for instance, that dilute aqueous solutions of sodium sulphate and potassium nitrate are mixed, it is readily seen that no appreciable change in the nature of the solution should occur, for potassium sulphate and sodium nitrate, the formation of which might be anticipated, are dissociated to as great an extent as the salts first mentioned, and all four salts are almost completely dissociated in dilute solution. Accordingly, no thermal effect would be expected to accompany the mixing of the solutions, and none is, in fact, observed.

In general, ions possess an enormously greater degree of reactivity than non-ionised molecules. The readiness and rapidity with which acids, bases, and salts react are in marked contrast to the sluggishness with which many reactions between organic substances proceed. The subject of inorganic qualitative analysis is concerned almost exclusively with the *reactions of ions*. An aqueous solution of hydrogen chloride, for instance exhibits the properties associated with hydrogen ions and also those associated with chlorine ions, and therefore its degree of reactivity towards other substances is quite different from that of a solution of hydrogen chloride in benzene or liquid hydrogen chloride The degree of electrolytic dissociation of hydrogen chloride in the benzene solution or in the liquefied gas is exceedingly small, and in these media iron, sodium, and calcium carbonate are scarcely acted upon; but aqueous hydrogen chloride attacks these substances with the greatest readiness[1]

The conclusion that the reactions of electrolytes are in general the reactions of their ions is of great importance, for it is natural to attribute the specific properties associated with acids to the presence of hydrogen ions, and those associated with bases to the presence of hydroxyl ions in their aqueous solutions. It is therefore to be expected that the extent to which these properties are manifested by an acid (or base) will depend upon the concentration of hydrogen (or hydroxyl) ions in solution; in short, that what may be termed the relative "strengths" of acids (or bases) may be inferred from the degrees of dissociation of the acids (or bases) in solutions that are comparable, *i.e.* are of the same normality. The stronger the acid (or base), the greater the degree of dissociation. The relative strengths of acids and bases thus deduced are in agreement with those derived from other considerations (*vide infra*, p. 225).

The dissociation theory accounts in a simple manner for the differences observed between double salts and complex salts. For example, sodium chloroplatinate, a complex salt, dissociates according to the scheme

$$Na_2PtCl_6 \rightleftharpoons 2Na^{\cdot} + PtCl_6'',$$

whereas the dissociation of astracanite (p. 201), a double salt, takes place as follows:—

$$Na_2SO_4.MgSO_4 \rightleftharpoons 2Na^{\cdot} + Mg^{\cdot\cdot} + 2SO_4''.$$

In the case of the first-named compound, the solution does not give the usual reactions of a chloride, since no chlorine ions are present in solution; the second compound, however, behaves as a mixture of the single salts. That the anion of sodium chloroplatinate is $PtCl_6''$ is shown by migration experiments (p. 206), the platinum migrating with the chlorine towards the anode. The recognition of the nature of complex salts by means of migration experiments is due to Hittorf (p. 207).

There is, however, no hard-and-fast line of division between complex salts and double salts; the difference must be looked upon not as one of kind, but only one of degree. It must be supposed, for instance, that the anion $PtCl_6''$ dissociates further, thus:—

$$PtCl_6'' \rightleftharpoons Pt^{\cdot\cdot\cdot\cdot} + 6Cl',$$

though only to a very minute extent, while the possibility of the existence of complex ions in astracanite solutions, such as $Mg(SO_4)_2''$ perhaps, must be recognised, though their concentration must be quite small. Examples are known in which each stage of the ionisation must be regarded as taking place to an appreciable extent, *e.g.* $K_2Cd(CN)_4$:—

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[1] An admirable account of the ionic theory, with particular reference to its applications in qualitative analysis, is given by Stieglitz, *Qualitative Chemical Analysis*, 2 vols. (The Century Co., New York, 1911; Bell & Sons, London, 1914); see also Ostwald, *Scientific Foundations of Analytical Chemistry*, translated by M'Gowan (Macmillan & Co., 1908).

$$K_2Cd(CN)_4 \rightleftharpoons 2K^{\cdot} + Cd(CN)_4'',$$
$$Cd(CN)_4'' \rightleftharpoons Cd^{\cdot\cdot} + 4(CN)'.$$

The relative stabilities of complex ions is a matter of great importance in analysis.

Application of the Laws of Chemical Equilibrium.—The laws of chemical equilibrium were applied to the study of ionic reactions almost as soon as Arrhenius' theory appeared, each kind of ion present in solution being regarded as a distinct molecular species, behaving as a normal solute. The undissociated molecules and the ions of an ionogen[1] in aqueous solution constitute a system in equilibrium, and the state of equilibrium alters with change of concentration. In reactions between ionogens, equilibrium is established with great rapidity.

In the case of a uni-univalent salt, which dissociates thus,

$$AB \rightleftharpoons A^{\cdot} + B',$$

the condition of equilibrium will be

$$\frac{[A^{\cdot}] \times [B']}{[AB]} = K,$$

where a bracketed formula, as usual, denotes the equilibrium concentration of the substance having that formula. If one gram-molecule of AB is dissolved in v litres of water, and the fraction dissociated is γ, then

$$[A^{\cdot}] = [B'] = \frac{\gamma}{v}, \quad [AB] = \frac{1-\gamma}{v},$$

and hence

$$\frac{\gamma^2}{(1-\gamma)v} = K,$$

where K denotes the *ionisation constant* in the usual units.

The condition of equilibrium that would similarly be expected for other types of ionogens is easily obtained. Thus, in the case of lanthanum sulphate,

$$La_2(SO_4)_3 \rightleftharpoons 2La^{\cdot\cdot\cdot} + 3SO_4'',$$

it would be anticipated that

$$\frac{[La^{\cdot\cdot\cdot}]^2 \times [SO_4'']^3}{[La_2(SO_4)_3]} = K,$$

leading to the relation

$$\frac{\gamma^5}{(1-\gamma)v^4} = K'.$$

It may be stated at once that the equations thus deduced, and which connect the degree of dissociation of an electrolyte with the concentration, are not even approximately correct representations of the experimental results for salts, or for acids and bases that are dissociated to more than a few per cent. in dilute solution.[1] In the case of weak acids and bases, however, these equations represent the facts extremely well.

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[1] *I.e.* a substance that dissociates into ions in solution.

In the case of a weak dibasic acid, such as carbonic acid, which dissociates in stages, the relationships

$$\frac{[H^\cdot] \times [HCO_3']}{[H_2CO_3]} = K_1 \text{ and } \frac{[H^\cdot] \times [CO_3'']}{[HCO_3']} = K_2$$

are found to hold good, K_1 and K_2 being called the *primary* and *secondary* ionisation constants of carbonic acid. In like manner there are three ionisation constants corresponding to the three stages of dissociation of orthophosphoric acid, etc.

The ionisation constants of a number of weak acids and bases are given in the following table:—[2]

Acid or Base.	Temp °C.	Equilibrium Ratio.	K.
Phosphoric acid . .	18	$[H^\cdot] \times [H_2PO_4']/[H_3PO_4]$	1×10^{-2}
	18	$[H^\cdot] \times [HPO_4'']/[H_2PO_4']$	2×10^{-7}
	18	$[H^\cdot] \times [PO_4''']/[HPO_4'']$	1×10^{-13}
Nitrous acid . . .	25	$[H^\cdot] \times [NO_2']/[HNO_2]$	5×10^{-4}
Acetic acid . . .	25	$[H^\cdot] \times [CH_3CO_2']/[CH_3COOH]$	$1{\cdot}8 \times 10^{-5}$
Carbonic acid . . .	18	$[H^\cdot] \times [HCO_3']/[H_2CO_3]$ *	3×10^{-7}
	25	$[H^\cdot] \times [CO_3'']/[HCO_3']$ *	7×10^{-11}
Hydrogen sulphide . .	18	$[H^\cdot] \times [HS']/[H_2S]$	9×10^{-8}
	25	$[H^\cdot] \times [S'']/[HS']$	1×10^{-15}
Boric acid . . .	25	$[H^\cdot] \times [H_2BO_3']/[H_3BO_3]$	7×10^{-10}
Hydrocyanic acid . .	25	$[H^\cdot] \times [CN']/[HCN]$	7×10^{-10}
Ammonium hydroxide .	25	$[NH_4^\cdot] \times [OH']/\{[NH_4OH] + [NH_3]\}$ †	$1{\cdot}8 \times 10^{-5}$
Hydrazine . . .	25	$[N_2H_5^\cdot] \times [OH']/\{[N_2H_5OH] + [N_2H_4]\}$ †	3×10^{-6}

* These solutions contain carbon di-oxide as well as carbonic acid molecules and ions. Hence the value for K is really much too low (Thiel and Strohecker, *Ber.*, 1914, **47**, 945).

† These solutions contain ammonia and hydrazine, in addition to the ions of the hydroxides and the undissociated hydroxide molecules.

Referring again to the equation (p. 222)

$$\frac{\gamma^2}{(1-\gamma)v} = K,$$

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[1] It is beyond the scope of this book to enter into a discussion of the causes of this disagreement; there are, however, good reasons why ionic equilibria should not be expected to conform to the law of chemical equilibrium except at very small concentrations. See Stieglitz, *opus cit.*, p. 108; Walker, *Nature*, 1911, **87**, 296. It is possible to express the variation of γ with the dilution by empirical formulæ. See Rudolphi, *Zeitsch. physikal. Chem.*, 1895, **17**, 385; Van't Hoff, *ibid.*, 1895, **18**, 300; Storch, *ibid.*, 1896, **19**, 13; M'Dougall, *J. Amer. Chem. Soc.*, 1912, **34**, 855; Kraus and Bray, *ibid.*, 1913, **35**, 1315; Kendall, *Trans. Chem. Soc.*, 1912, **101**, 1275; *Medd. K. Vet. Nobelinstitut*, 1913, **2**, No. 38; *J. Amer. Chem. Soc.*, 1914, **36**, 1069; Partington, *Trans. Chem. Soc.*, 1910, **97**, 1158.

[2] For further data and references see Landolt-Bornstein, *Physikalisch-Chemische Tabellen* (Berlin, 3rd ed., 1912), p. 1132; Noyes, *J. Amer. Chem. Soc.*, 1910, **32**, 860; Stieglitz, *opus cit.*, pp. 104, 106.

which is called *Ostwald's Dilution Law*, it is seen that when half the electrolyte is dissociated, $1/2v$ is equal to K. Using the value given above for acetic acid, it follows that one gram-molecule of acetic acid must be diluted with about 30,000 litres of water before half the acid is dissociated; and that an even greater dilution is necessary for those substances with ionisation constants smaller than acetic acid. Hence, comparing electrolytes at the same (molecular) concentration, the order of increasing dissociation is also the order of increasing ionisation constants. The relative strengths of weak acids (and bases) may be accordingly recognised by a comparison of their ionisation constants. The small degree of dissociation of the acids and bases mentioned in the preceding table will be readily perceived from the values of K there given; acetic acid, for instance, in decinormal solution (v equal to 10) is dissociated only to the extent of 1·3 per cent.

It should be carefully borne in mind that salts derived from weak acids or bases are largely dissociated in solution, sodium acetate, for instance, being comparable with sodium chloride in this respect. A simple means of diminishing the acidic properties of a weak acid or the basic properties of a weak base is therefore possible; namely, to add a salt with a common ion, as, for instance, sodium acetate to acetic acid, and ammonium chloride to ammonium hydroxide. In the latter case, the concentration of ammonium ions is enormously increased, and in virtue of the relationship

$$\frac{[NH_4^{\cdot}] \times [OH']}{[NH_4OH]} = K,$$

the concentration of hydroxyl ions must decrease. In other words, the degree of dissociation of ammonium hydroxide is diminished, and that to a very great extent, since, as the concentration of undissociated ammonium hydroxide only varies by 1 or 2 per cent., an n-fold increase of concentration in ammonium ions leads to an n-fold decrease in concentration of hydroxyl ions. This principle is frequently employed in analysis.

The equilibrium between a solid salt and a liquid which, besides containing some of the salt in solution, also contains other electrolytes, is of great importance. It was originally supposed[1] that in such a system, at constant temperature, while the concentrations of the ions of the salt could be altered by the addition of other electrolytes, the concentration of the undissociated salt in the liquid remained constant. This supposition, combined with the further one that the ionisation of the salt is expressed by the law of chemical equilibrium, leads to the following condition for equilibrium between the solid salt and the liquid phase; *the product of the ion concentrations, each raised to the power corresponding to the number of that kind of ion formed by the dissociation of one molecule of the salt, is a constant.* An example will make this clear. If the solid salt is calcium phosphate $Ca_3(PO_4)_2$, the law of equilibrium gives

$$[Ca^{\cdot\cdot}]^3 \times [PO_4''']^2 = K[Ca_3(PO_4)_2]$$

for the ionic equilibrium in the liquid phase; and in accordance with the first assumption, $[Ca_3(PO_4)_2]$ is a constant for equilibrium between the solid and liquid phases. Hence

$$[Ca^{\cdot\cdot}]^3 \times [PO_4''']^2 = \text{constant}.$$

This constant is called the *solubility-product* of the salt at the temperature in question.

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[1] Nernst, *Zeitsch. physikal. Chem.*, 1889, 4, 372.

The method of deriving the principle of the solubility-product just outlined is that by which the relationship was first deduced. Each of the assumptions there mentioned is now known to be incorrect. It is, however, not necessary to assume so much in order to deduce the principle, which follows from the assumptions that the ions behave as normal solutes, and that the nature of the solvent is not changed by added substances.[1] As a matter of experiment, the principle is found to hold good only for dilute solutions in which the total electrolyte concentration is not greater than 0·3 gram-equivalent per litre, and hence can only be applied to sparingly soluble substances.[2] Salts ordinarily classed as insoluble, and in particular those met with as precipitates in quantitative analysis, are characterised by extremely small solubility-products.

When the product of the concentrations of the ions of a salt in a solution exceeds the solubility-product of the salt, precipitation of that salt occurs until the solubility-product is reached. It immediately follows that the solubility of a salt is less in a solution of a salt possessing a common ion than it is in pure water. For example, the amount of chlorine left in solution, when a solution of a chloride is precipitated with silver nitrate in moderate excess, is barely perceptible, although the solubility of silver chloride in pure water is quite appreciable.[3] That is to say, the solubility of silver chloride has been diminished by the presence of silver nitrate in solution.

A salt passes into solution when the product of the concentrations of its ions in the solution is made less than the solubility-product. Two examples may be given. The organic acid oxalic acid is a weak acid and dissociated to a much less degree than its calcium salt at the same concentration. The calcium salt is almost insoluble in water. When hydrochloric acid is added to it, the anion of oxalic acid is removed almost entirely from the solution, since it unites with hydrogen ions, present in great excess, to form undissociated oxalic acid. Hence, the solubility-product of calcium oxalate not being maintained, solid salt passes into solution until the solubility-product is again reached. The increase in concentration of the calcium ions in the solution is such that calcium may be readily detected therein by the usual reactions, *i.e.* calcium oxalate is soluble in hydrochloric acid.

Silver cyanide is very sparingly soluble in water. The addition of potassium cyanide solution would, in the light of the preceding discussion, be expected to diminish its solubility, but it is found to dissolve the precipitate. The explanation is that the reaction

$$Ag^{\cdot} + 2CN' \rightleftharpoons Ag(CN)_2'$$

occurs in the solution, and since the complex ion $Ag(CN)_2'$ is a stable ion, the concentration of the silver ions in solution is reduced to a very minute quantity. Silver chloride accordingly dissolves; the complex salt $K[Ag(CN)_2]$ can be crystallised out from the solution.

Strengths of Acids and Bases.—The expressions "strong" and "weak" are frequently applied in order to describe the relative chemical activities of acids and of bases. In contrasting an acid such as hydrochloric with another such as hydrosulphuric, it is easy from chemical considerations to decide that the first is "stronger" than the second; the problem of comparing the relative strengths of, say, hydrochloric and sulphuric acids, is more difficult.

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[1] Washburn *J. Amer Chem. Soc.*, 1910, 32, 488.

[2] Stieglitz, *ibid.*, 1908, 30, 946.

[3] Richards and Wells, *J. Amer. Chem. Soc.*, 1905, 27, 481.

In order to arrive at a quantitative estimation of the relative strengths of acids, equivalent amounts of two acids may be allowed to compete for a quantity of a base insufficient to combine with both completely, and the ratio in which the base is shared by the acids determined. The relative strengths of the acids are regarded as proportional to the amounts of base they appropriate. The method may be carried out in practice by adding one equivalent of an acid to one equivalent of a salt of another acid, and determining the amount of the second acid displaced from combination by the first. In effecting the necessary measurements, which are generally physical in character,[1] one condition must be fulfilled: the acids and salts must remain entirely in solution and nothing escape from the liquid either as gas or solid (precipitate). Otherwise the results are vitiated by volatility or solubility influences.

Approximate results were obtained by Thomsen[2] from thermal measurements, but Ostwald's results, deduced from density measurements[3] were more accurate. The experiments were carried out at a common temperature, and the solutions of acids and bases used contained one gram-equivalent of reagent in a kilogram of solution. By mixing equal weights of a solution of an acid and a base, a solution of a salt was obtained. A numerical example concerning hydrochloric and dichloracetic acids will serve to illustrate the method. The respective volumes of two kilograms of sodium chloride and sodium dichloracetate solutions were 1958·275 and 1916·714 c.c.; those of one kilogram of hydrochloric acid and dichloracetic acid solutions, 982·406 and 947·377 c.c. On mixing the hydrochloric acid and sodium dichloracetate solutions, the volume would be 982·406 + 1916·714, or 2899·120 c.c. if no change occurred, and 947·377 + 1958·275, or 2905·652 if the dichloracetic acid were entirely displaced. The volume actually observed was 2901·220 c.c. Now

$$2904{\cdot}220 - 2899{\cdot}120 = 5{\cdot}100$$

and

$$2905{\cdot}652 - 2899{\cdot}120 = 6{\cdot}532\,;$$

hence it is inferred that 5·10/6·53 or 78 per cent. of the dichloracetic acid is displaced, and the relative strengths of hydrochloric and dichloracetic acids are as 78 to 22.

The relative strengths of acids as determined in this manner are independent of the nature of the base chosen. That the order in which the acids are arranged by this method is really the order of what are to be regarded as their "strengths" is indicated by the fact that the same order is arrived at when the activities of acids are compared in other ways, *e.g.* by Thomsen's thermal method; by observing the rate at which they cause the "inversion" of sucrose to proceed (p. 184), by determining their respective abilities to effect the solution of salts like calcium oxalate and barium chromate, etc.

It is found that when acids are arranged in the order of their relative strengths, they are also arranged in order with respect to their degrees of dissociation, the strongest acids being most fully dissociated. This result is readily intelligible (see p. 224). Moreover, it is possible, if the dissociation theory be accepted, to calculate the relative strengths of two weak acids, since they follow the "dilution law." The result arrived at is that equivalent quantities of the two acids share a quantity of base sufficient to neutralise only one acid in the ratio of the square roots of the dissociation constants of the acids, and this result is confirmed by experiment.[1]

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[1] A chemical method of limited application has been devised by Friend and Marshall (*Trans. Chem. Soc.*, 1914, **105**, 2776), based on the observation that the amount of alkali necessary to prevent an acid from corroding iron is a function of the strength of the acid.

[2] Thomsen, *Pogg. Annalen*, 1854, **91**, 8 ; 1869, **138**, 65 ; *Phil. Mag.*, 1870, [iv.], **39**, 410.

[3] Ostwald, *J. prakt. Chem.*, 1877, (ii.), **16**, 385 ; 1878, **18**, 323.

The relative strengths of bases may be compared by methods similar to those employed for acids. The weakness of ammonium hydroxide in comparison with sodium hydroxide was shown by Berthelot from thermal measurements.[2] The order of relative strengths of bases is also found to be that anticipated from their degrees of dissociation.

The hydroxides of the divalent metals such as zinc, nickel, magnesium, etc., and of the trivalent metals such as iron, aluminium, chromium, etc., are almost insoluble in water, but the fact that they are *weak* bases is shown by the hydrolysis of the salts they form with strong acids. A number of these hydroxides are amphoteric, and must accordingly be regarded as behaving as weak *acids* as well. For example, aluminium hydroxide is regarded as dissociating, in its (very dilute) aqueous solution, as a base, thus:—

$$Al(OH)_3 \rightleftharpoons Al^{\cdot\cdot\cdot} + 3OH'$$

and as an acid, thus:—

$$Al(OH)_3 \rightleftharpoons H^{\cdot} + AlO_2' + H_2O,$$

in each case the degree of dissociation being slight. It follows that self-neutralisation should occur between basic and acidic aluminium hydroxide; but since salts formed from weak acids and weak bases are hydrolysed to a very considerable degree in solution, the extent to which self-neutralisation occurs is very small.[3]

Salt Hydrolysis or Hydrolytic Decomposition.—Ordinary distilled water is an extremely poor electrolyte, and its conductivity continuously decreases as it is subjected to more and more purification. Pure water has therefore been supposed by some chemists to be devoid of conductivity. This view is, however, not usually accepted, and, on the supposition that the pure liquid has a small conductivity and is therefore slightly dissociated, some half a dozen different methods have been employed to determine the degree of dissociation.[4] Considering the smallness of the quantity to be determined, the various results agree remarkably well. The dissociation appears to follow the course $H_2O \rightleftharpoons H^{\cdot} + OH'$, any further dissociation of the hydroxyl $OH' \rightleftharpoons H^{\cdot} + O''$ being quite negligible. The concentration of hydrogen ions $[H^{\cdot}]$ in pure water, then, is equal to that of the hydroxyl ions $[OH']$; the value is $1{\cdot}1 \times 10^{-7}$ gram-ions per litre at 25°, and increases rapidly with rise of temperature. Considering the equilibrium $H_2O \rightleftharpoons H^{\cdot} + OH'$, it follows, since $[H_2O]$ cannot appreciably alter, that the relationship

$$[H^{\cdot}] \times [OH'] = \text{constant } (1{\cdot}2 \times 10^{-14} \text{ at } 25^{\circ})$$

holds in pure water, and also in *all dilute aqueous solutions.*

The dissociation of water, slight though it be, is sufficient to account for the occurrence of *hydrolysis* in aqueous solutions of many salts, *i.e.* partial decomposition of the salt into acid and base, brought about by water. The change

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[1] Arrhenius, *Zeitsch. physikal. Chem.*, 1890, **5**, 1.

[2] Berthelot, *Compt. rend.*, 1880, **91**, 139.

[3] Walker, *Zeitsch. physikal. Chem.*, 1904, **49**, 82; 1905, **51**, 706. Heyroth (*J. Amer. Chem. Soc.*, 1916, **38**, 57) regards multiple ionisation as a phenomenon common to all electrolytes.

[4] Hudson, *J. Amer. Chem. Soc.*, 1909, **31**, 1136; references to the methods used by others are there given.

$$\text{acid} + \text{base} \rightleftharpoons \text{salt} + \text{water}$$

is, in fact, reversible; and provided either the acid or the base (or both) be *very weak*, the reversibility of the change is sufficiently marked to be readily observed. Examples have been known for years. Thus, aqueous solutions of sodium (or potassium) cyanide, borate, and sulphide possess the specific properties associated with bases to varying degrees, and give alkaline reactions towards the common indicators; while the presence of free acid is easily recognised in solutions of ammonium chloride, ferric chloride, zinc nitrate, etc.

The methods by which the degrees of hydrolysis of salts are determined cannot be entered into, but the explanation of the phenomenon by means of the dissociation theory[1] may be outlined, taking potassium cyanide as an example. This salt is largely dissociated in aqueous solution, $KCN \rightleftharpoons K^{\cdot} + CN'$, and since there are also present the ions $H^{\cdot}$ and OH', it is necessary to consider to what extent the changes $K^{\cdot} + OH' \rightleftharpoons KOH$ and $H^{\cdot} + CN' \rightleftharpoons HCN$ occur in the solution. Formation of non-ionised potassium hydroxide and prussic acid must occur, but, while the first-named substance cannot be thus produced in any appreciable quantity, it is clear that the second will be formed to a considerable extent, owing to the extremely small degree of dissociation of that substance. As hydroxyl ions and hydrogen ions are used up in these changes, further supplies are produced by the dissociation of more water, since the equilibrium $H_2O \rightleftharpoons H^{\cdot} + OH'$ is destroyed; and it will be observed that the hydrogen ions are used up to a much greater extent than the hydroxyl ions, which therefore accumulate in solution. The increase in the value of $[OH']$, with the consequent diminution of $[H^{\cdot}]$, goes on until the value of $[H^{\cdot}] \times [CN']/[HCN]$ reaches the ionisation constant of prussic acid, when equilibrium is attained. The result is, therefore, that water is used up in decomposing a certain fraction of the potassium cyanide, producing prussic acid, almost entirely undissociated, in the solution, together with an equivalent amount of potassium hydroxide, almost completely dissociated. In decinormal solution at 25°, the extent of hydrolysis amounts to 1·3 per cent.,[2] and the solution has a pronounced alkaline reaction.[3]

The preceding example illustrates the case of the hydrolysis of the salt of a weak acid and strong base; it may be left to the reader to show that the salt of a strong acid and weak base should have an acid reaction in solution, that the hydrolysis of the salt of a weak acid and weak base should be quite pronounced, and that the hydrolysis of the salt of a strong acid and strong base should be inappreciable.

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[1] First given, and mathematically developed, by Arrhenius, *Zeitsch. physikal. Chem.*, 1890, 5, 16.

[2] Shields, *Zeitsch. physikal. Chem.*, 1893, **12**, 167; Madsen, *ibid.*, 1901, 36, 290.

[3] Since, in terms of the ionic theory, the specific properties of acids and bases are the properties of hydrogen and hydroxyl ions respectively, water, in which these ions are present in equal concentrations, is considered to be *neutral* in reaction. A solution is then regarded as having an *acid* or *alkaline* reaction according as the concentration of the hydrogen ions exceeds that of the hydroxyl ions in solution or vice versa. Acidity and alkalinity as indicated by the commonly employed *indicators*, e.g. *litmus, methyl-orange, and phenolphthalein*, usually, but not always, agree with these definitions.

CHAPTER VII.

THE DETERMINATION OF ATOMIC WEIGHTS AND EQUIVALENT OR COMBINING WEIGHTS.

Introductory.—The modern system of atomic weights is essentially that due to Cannizzaro, whose system of atomic weights, based on Avogadro's Hypothesis, was published in 1858. An account of the various systems of atomic weights that were in vogue during the first half of last century has been already given in Chap. I.

Of the earlier methods for calculating atomic weights, those based on the Law of Dulong and Petit and the Principle of Isomorphism supply valuable corroborative evidence as to the validity of the results deduced by the fundamental method, viz. the application of Avogadro's Hypothesis, and enable the atomic weights of a number of metals to be deduced where Avogadro's Hypothesis cannot be applied for want of the necessary data. In the case of the inert gases, none of these methods is applicable, and advantage is taken of the results obtained by a study of their specific heats.

The numerical results obtained by the application of the preceding methods are, in general, only approximate; this arises in consequence of (i.) experimental errors inherent in the determination of molecular weights from vapour densities, etc. (ii.) deviations of gases and vapours from the laws of the "perfect" gas, and (iii.) the approximate character of Dulong and Petit's Law. To arrive at the exact values, two methods are available. The first is a chemical method, and consists in selecting for the atomic weights of the elements those multiples of their chemical equivalents (or combining weights) which most nearly approach the approximate values obtained for the atomic weights. The equivalents may, by suitable experimental methods, be determined with great precision, and the selection of the correct multiples of these values offers no difficulty, even with approximate atomic weight values several per cent. in error.

The second method is purely physical, and has been developed since about 1890. It has been seen in Chap. IV. that it is possible, from accurate measurements of gaseous densities and compressibilities, to deduce the molecular weights of certain gases with a high degree of accuracy. Since the molecular formulæ of the gases may be readily determined, their exact molecular weights may be utilised in deducing the exact atomic weights of their constituents. For example, the atomic weight of carbon follows readily from the molecular formula and exact molecular weight of carbon monoxide or dioxide, whilst from the corresponding data for methane, the atomic weight of carbon may be inferred if that of hydrogen be assumed. This method is only of limited applicability, but has given a number of results in good agreement with those deduced from the most accurate measurements of combining weights.

Reverting to the chemical method of determination of accurate atomic weights, it should be explained that the following is the plan actually adopted. The formulæ of the compounds studied are assumed. This may be done since the formulæ can be derived from approximate atomic weight values. Supposing then, as an example, that the atomic weight of arsenic is sought; a known weight of silver arsenate may be heated in hydrogen chloride until it is completely converted into silver chloride, and the latter weighed. Knowing the formulæ to be Ag_3AsO_4 and $AgCl$, the ratio, weight of arsenate : weight of chloride, is clearly the ratio of the molecular weight of silver arsenate to three molecular weights of silver chloride, *i.e.* $Ag_3AsO_4 : 3AgCl$. If, then, the atomic weights of silver, chlorine, and oxygen be known (107·88, 35·46, and 16·00 respectively), the atomic weight of arsenic (x) is readily found. For

$$\frac{\text{Wt. of silver arsenate}}{\text{Wt. of silver chloride}} = \frac{(3 \times 107\cdot88) + x + (4 \times 16)}{3(107\cdot88 + 35\cdot46)}.$$

Since the preceding is a typical example of the manner in which accurate atomic weights are derived by the chemical method, it will not be difficult to understand how it is that certain atomic weights are of fundamental importance, entering as they so frequently do into the calculation of other atomic weights. The fundamental atomic weights are those of oxygen (standard), silver, chlorine, bromine, iodine, sulphur, nitrogen, carbon, sodium, and potassium. A large amount of accurate work has been carried out whereby it has been possible to derive the fundamental atomic weights with a high degree of accuracy.[1]

Of the numerous chemists who have, in the past, interested themselves in the accurate determinations of atomic weights, special mention must be made of Marignac and Stas.[2] The values adopted for many years for the fundamental atomic weights were practically identical with those derived by Stas, whose laborious and painstaking work was regarded as being of extreme accuracy. It is now known that the work of Stas was affected by numerous slight errors, and the fundamental atomic weights have in consequence been carefully revised. This task of revision, and also the determination of numerous other atomic weights, has been carried out very largely by Professor T. W. Richards, of Harvard University, and his numerous collaborators.[3]

The atomic weights in use represent *relative* values, referred to an arbitrary standard; the *actual* weights of atoms are not known with certainty, and do not concern the chemist. Dalton originally selected hydrogen, which has the smallest atomic weight, as the standard, and called its atomic weight unity; but the inconvenience of this choice was early recognised. The number of stable hydrides the compositions of which are accurately known, is small, and hence combining weights are usually measured with respect to oxygen or a halogen, and must be referred indirectly to hydrogen. In each indirect comparison the experimental errors attached to the antecedent data affect the final result; and the value for the ratio oxygen : hydrogen, which entered into the calculation of many combining weights, was for years in serious error. Even to-day, according to Noyes,[1] a slight uncertainty is attached to the value at present adopted, although for most purposes any error involved is negligibly small.

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[1] For a discussion of the fundamental atomic weights, see F. W. Clarke, *A Recalculation of the Atomic Weights* (Smithsonian Miscellaneous Collections, vol. liv., No. 3), 3rd edition, 1910.

[2] For their work on atomic weights, see Marignac, *Œuvres complètes* (Geneva, 2 vols., 1902); and Stas, *Œuvres complètes* (Brussels, 3 vols., 1894).

[3] The collected papers of Richards and his collaborators are published in a volume entitled *Experimentelle Untersuchungen über Atomgewichte* (Voss, Leipzig, 1909). For a summary, see Richards, *Carnegie Institution Publications*, No. 125 (1910); *J. Chim. phys.*, 1908, 6, 92.

Berzelius, guided by considerations of practical convenience, employed the standard *oxygen = 100*, and this was adopted for many years. About the time of Dumas' syntheses of water,[2] the hydrogen scale was revived; according to the results of Dumas, O = 15·96 on this scale, and he regarded the value 16 as probably correct. The suggestion, made later by Stas, to adopt as standard *oxygen = 16*, therefore received little support, since it would have involved very little change in the atomic weight values at that time in use.

The question of a suitable standard was again raised when, during the period 1888–95, it became clear that, on the hydrogen scale, the atomic weight of oxygen is 15·88 and not 15·96 as had been previously supposed. Although the retention of hydrogen as unity has been strongly favoured by Lothar Meyer, Seubert, Clarke, and others, and still has its supporters, the standard **oxygen = 16**, advocated so warmly by Ostwald, is now adopted by international agreement. A very practical advantage of this scale is that the atomic weights of a number of common elements may be represented by whole numbers without appreciable error. It is nevertheless true that a large number of atomic weight measurements are only referred indirectly to oxygen, the atomic weight of a halogen being usually involved in the calculation.[3]

Determination of Atomic Weights from Analyses of Gaseous Compounds.

The atom of an element is the smallest part of it that occurs in the molecules of its compounds. The method to be followed in seeking its atomic weight is readily understood in the light of this definition. Two series of values are necessary: (i.) the molecular weights of its compounds, which may be obtained in a variety of ways (see Chap. IV.); and (ii.) the amount of the element contained in each of these molecules. The latter series of values may be deduced from the results of chemical analysis and the values found for the molecular weights; the required atomic weight may then be determined by inspection. "The different weights of one and the same element contained in the various molecules are always whole multiples of one quantity, which is justly called the atom because it invariably enters the compounds without division" (Cannizzaro). The atomic weight is, in fact, the greatest common measure of the magnitudes (ii.).

The accompanying tables illustrate the application of this method to th determination of the atomic weights of oxygen, hydrogen, carbon, and phosphorus. In five columns are given successively: (i.) the name of the substance utilised;[1] (ii.) the density (*d*) of its vapour, compared with that of oxygen under the same conditions of temperature and pressure;[2] (iii.) the percentage (*p*) of the element, the atomic weight of which is sought; (iv.) the molecular weight ($32d$) of the substance referred to that of oxygen as 32, and calculated from (ii.); and (v.) the weight ($32dp/100$) of the element present in the molecular weight of the substance, calculated from (iii.) and (iv.).

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[1] Noyes, *J. Amer. Chem. Soc.*, 1907, 29, 1718; *cf.* Morley, *Smithsonian Contribution to Knowledge*, 1895, 29, No. 980.

[2] Dumas, *Compt. rend.*, 1842, 14, 537.

[3] For a full account of the various standards that have been suggested and used, see Miss Freund, *The Study of Chemical Composition* (Cambridge University Press, 1904, pp. 188–192.

OXYGEN.

I.	II.	III.	IV.	V.
Water	0·5631	88·78	18·02	16·00
Nitric oxide . . .	0·9378	53·32	30·01	16·00
Alcohol	1·4394	34·73	46·06	16·00
Ether	2·316	21·58	74·10	16·00
Oxygen	1·0000	100·00	32·00	32·00 = 2 × 16·00
Carbon dioxide . . .	1·3750	72·72	44·00	32·00 = 2 × 16·00
Ozone	1·5000	100·00	48·00	48·00 = 3 × 16·00
Osmium tetroxide . .	7·965	25·11	254·9	64·00 = 4 × 16·00

HYDROGEN.

I.	II.	III.	IV.	V.
Hydrogen chloride . .	1·1397	2·77	36·47	1·01
Hydrogen cyanide . .	0·8444	3·74	27·02	1·01
Water	0·5631	11·21	18·02	2·02 = 2 × 1·01
Hydrogen	0·0631	100·00	2·02	2·02 = 2 × 1·01
Ammonia	0·5325	17·78	17·04	3·03 = 3 × 1·01
Methane	0·5012	25·19	16·04	4·04 = 4 × 1·01
Alcohol	1·439	13·15	46·06	6·06 = 6 × 1·01

CARBON.

I.	II.	III.	IV.	V.
Carbon monoxide . . .	0·8750	42·86	28·00	12·00
Carbon dioxide . .	1·3750	27·28	44·00	12·00
Methane	0·5012	74·81	16·04	12·00
Alcohol	1·439	52·12	46·06	24·00 = 2 × 12·00
Ether	2·316	64·78	74·10	48·00 = 4 × 12·00
Benzene	2·439	92·23	78·06	72·00 = 6 × 12·00

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[1] The lists of volatile compounds are merely illustrative, not exhaustive.

[2] The "theoretical" value is given, from which the accurate molecular weight may be obtained.

PHOSPHORUS.

	II.	III.	I.	
Phosphine	1·0647	91·11	34·07	31·04
Phosphorus trichloride . .	4·294	22·59	137·1	31·04
,, pentafluoride .	3·939	21·63	126·0	31·04
,, pentasulphide .	6·951	27·91	222·4	62·08 = 2 × 31·04
Phosphorous anhydride . .	6·880	56·40	220·2	124·2 = 4 × 31·04
Phosphorus	3·880	100·00	124·2	124·2 = 4 × 31·04

From the results contained in the tables, the atomic weights of oxygen, hydrogen, carbon, and phosphorus are seen to be 16·00, 1·01, 12·00, and 31·04 respectively. The selection of 32 as the molecular weight of oxygen, on the assumption that the molecule of oxygen is diatomic, thus receives confirmation.

It will be observed that in order to determine the atomic weight of an element, it is not necessary to know its vapour density; carbon affords an illustration of this point. When the element is volatile, as, for instance, in the cases of oxygen, hydrogen, and phosphorus previously cited, the vapour density merely serves to indicate the atomicity of the molecule. A knowledge of the atomic weight of an element may, in fact, precede its isolation in the free state, as was the case with fluorine.

The method of determining the atomic weight of an element described in this section ceases to be applicable (i.) when no compounds of the element are available, *e.g.* the inert gases; and (ii.) when the element forms no volatile compounds; in such cases the molecular weights of the compounds can rarely be found. Instances are afforded by a number of metals, *e.g.* the metals of the alkaline earths. The probability that the atomic weight of an element has been correctly chosen by this method clearly depends upon the number of compounds it furnishes, the molecular weights of which can be determined. The atomic weights of the non-metals, which form numerous volatile compounds, are therefore known with practical certainty; but owing to the smaller number of volatile compounds supplied by the metals, their atomic weights, deduced by this method alone, cannot be accepted with such confidence. In various cases, however, metallic derivatives are known, the molecular weights of which in solution can be determined by the methods described in Chap. IV., thereby supplementing the data derived from vapour-density measurements; whilst other methods of deducing atomic weights are available (see next section), which confirm the results derived by the application of Avogadro's principle.

DETERMINATION OF ATOMIC WEIGHTS BY APPROXIMATE METHODS.

Attention has already been drawn to the fact that the chemical equivalent or combining weights of the elements may be determined with great accurac by chemical methods. In order to select correct multiples of these equiva lents for the atomic weights of the corresponding elements, approximat determinations of the atomic weights may be made by the following methods:—

1. Determination of the specific heat of the element or of its compound and the application of laws such as those of Dulong and Peti Neumann and Kopp, to the result (see pp. 94-96).

2. Determination of the ratio of the two specific heats of the element in the gaseous form (see pp. 96–97).
3. A comparison of the general properties of the element with those predicted for hitherto undiscovered elements required to complete the Periodic Table (see p. 275).
4. A study of the crystalline form of the various compounds of the element and the application of Mitscherlich's Law of isomorphism (see p. 74).
5. Comparison of the transparencies of the elements to X-rays.

In 1901 Benoist[1] drew attention to the fact that the specific opacity of an element for the X-rays bears a simple relation to the atomic weight. In the case of compounds the specific opacity is an additive property, being the sum of the opacities of the constituent atoms. Hence, whether the element can be isolated in the free state or not, its opacity and approximate atomic weight are capable of being determined. The method has been applied to indium,[2] and the results show that the atomic weight of this element is 113·4 and not 75·6. The atomic weights of thorium and cerium have been similarly[3] fixed at 232 and 140·25 respectively, and for glucinum[4] the value 9·1 has been obtained.

6. In addition to the preceding five methods for arriving at the approximate values of the atomic weights of the elements, other methods are available, based upon spectroscopic measurements. In order to explain these it is necessary to discuss briefly the nature of series lines in spectra.[5]

In many spectra the lines have the appearance of being distributed at random. In others, however, there are lines which succeed each other in a regular manner so that their positions may be represented by formulæ. Such a collection of lines is called a *series*; in the series the lines become closer and less intense on passing in the direction from red to violet. Usually a number of series co-exist in the same spectrum, and only in very few cases has it been found possible to represent *all* the observed lines as members of series. In discussing series it is more convenient to deal with the *wave number* (or "oscillation frequency") than with the wave-length (λ). The wave number (n) is $10^8/\lambda$, or the number of waves per centimetre; and it is usual to correct the value to vacuum.

In 1885 Balmer[6] discovered that the lines in the ordinary hydrogen spectrum could be represented with great accuracy by an equation of the type

$$n = \mathrm{N}(1/4 - 1/m^2),$$

where N is a constant and for m the successive integers 3, 4, 5, . . . are inserted. The value of N is found to be 109,675, and, as it is of fundamental importance, it is spoken of as the "universal constant" or as "Rydberg's constant," for reasons which will appear presently.

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[1] Benoist, *Compt. rend.*, 1901, **132**, 324 and 545.

[2] Benoist, *ibid.*, 1901, **132**, 772; see also INDIUM, Vol. IV. of this series.

[3] Benoist and Copaux, *Compt. rend.*, 1914, **158**, 689.

[4] Benoist and Copaux, *ibid.*, 1914, **158**, 859.

[5] The authors wish to express their thanks to Mr W. Jevons, B.Sc., for kind assistance in the preparation of this section. For further details the reader is referred to the report on "Series Lines in Spectra," in *Monthly Notices of Royal Astronomical Soc.*, 1914, **74**, 354; Fowler, The Bakerian Lecture, *Phil. Trans.*, 1914, **A**, **214**; *Nature*, 1914, **93**, 145; Baly, *Spectroscopy* (Longmans & Co., 2nd edition, 1912).

[6] Balmer, *Wied. Annalen*, 1885, [iii.], **25**, 80. According to the measurements of Curtis (*Proc. Roy. Soc.*, 1914, **A**, **90**, 605), however, the first six lines of the hydrogen spectrum are not exactly represented by Balmer's formula.

It is easy to see that N/4 is the "limit" or end of the series, corresponding to $m = \infty$. Denoting the "limit" (or "convergence frequency," as it is sometimes called) by n_∞, Balmer's equation may be written

$$n = n_\infty - \mathrm{N}/m^2.$$

The work of Rydberg[1] showed that a great many similar series occur in spectra. The series could not, however, be represented by Balmer formulæ, although very good representations could be obtained by equations of the type

$$n = n_\infty - \mathrm{N}/(m + \mu)^2.$$

In this equation N is the "universal constant" of value 109,675 ; n_∞ and μ are two other constants special to each series. The value of μ is usually fractional, and n_∞, which denotes the "limit" of the series, is no longer equal to N/4, as in Balmer's equation.

It may be stated at once that the Rydberg formulæ usually fail to represent series within the observational limits of error, and more exact formulæ have been devised. These differ from Rydberg's formula in that the expression $(m+\mu)^2$ is modified, (i.) by Ritz to $(m + a + \beta/m^2)^2$, (ii.) by Fowler and Shaw to $(m + \mu)^2 + a$, (iii.) by Hicks to $(m + a + \beta/m)^2$, and (iv.) by Paulson to $(m + \mu)^2 e^{\frac{b}{m^2}}$, where a and β and b are constants.[2] The formula of Ritz has the disadvantage that in some series (sharp series, *vide infra*) m does not have integral values, but has to be put equal to 2·5, 3·5, 4·5, etc. In the sequel Rydberg's formula will be used ; the necessary modifications to obtain the Ritz, Fowler and Shaw, Hicks, and Paulson equations will be obvious

In the general case three associated series are found in the same spectrum. They are referred to as the *Principal*, *Diffuse* (or 1st Subordinate), and *Sharp* (or 2nd Subordinate) series ; and the names are abbreviated to P, D, and S. The limits are denoted by $\mathrm{P}\infty$, $\mathrm{D}\infty$, and $\mathrm{S}\infty$ respectively. With the Rydberg formula the first line of a principal series is given when $m = 1$; with the subordinate series, when $m = 2$. The relationships between the three series are shown in fig. 73, which refers to the spectrum of lithium.

The equations to the P, D, S series may be written :—

$$\begin{array}{llll}
\mathrm{P.} & n = \mathrm{P}(m) = \mathrm{P}\infty - \mathrm{N}/(m + p)^2, & \text{where } m = 1, 2, 3, \ldots & \text{in succession.} \\
\mathrm{D.} & n = \mathrm{D}(m) = \mathrm{D}\infty - \mathrm{N}/(m + d)^2, & \quad ,, \quad m = 2, 3, 4, \ldots & \quad ,, \\
\mathrm{S.} & n = \mathrm{S}(m) = \mathrm{S}\infty - \mathrm{N}/(m + s)^2, & \quad ,, \quad m = 2, 3, 4, \ldots & \quad ,,
\end{array}$$

Several remarkable relationships have been discovered which connect these series, viz. (i.) $\mathrm{D}\infty = \mathrm{S}\infty$, (ii.) $\mathrm{P}\infty - \mathrm{D}\infty = \mathrm{P}(1)$, and (iii.) $\mathrm{S}(1) = -\mathrm{P}(1)$. From these relationships it follows that the series equations may be written :—

$$\begin{array}{rl}
& \mathrm{P}(m) = \mathrm{N}\left[1/(1 + s)^2 - 1/(m + p)^2\right], \text{ or } (1s - mp) \text{ for short,} \\
& \mathrm{D}(m) = \mathrm{N}\left[1/(1 + p)^2 - 1/(m + d)^2\right], \text{ or } (1p - md) \text{ for short,} \\
\text{and} & \mathrm{S}(m) = \mathrm{N}\left[1/(1 + p)^2 - 1/(m + s)^2\right], \text{ or } (1p - ms) \text{ for short.}
\end{array}$$

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[1] Rydberg, *K. Svenska Vet.-Akad. Handl.*, 1890, **23**, No. 11 ; *Paris International Reports*, 1900, **2**, 200. For a summary of the first of these papers, see Rydberg, *Phil. Mag.*, 1890, [v], **29**, 331.

[2] Ritz, *Physikal. Zeitsch.*, 1903, **4**, 406 ; 1908, **9**, 244, 521 ; *Ann. Physik*, 1903, [iv.], **12**, 264 ; 1908, [iv.], **25**, 660 ; *Astrophys. J.*, 1908, **28**, 237 ; Fowler and Shaw, *Proc Roy. Soc.*, 1903, **71**, 419 ; Hicks, *vide infra* ; Paulson, *Lunds Univ. Arsskrift*, N.F. Afd. 2, 1914, **10**, No. 12. See Halm, *Trans. Roy. Soc. Edin.*, 1904, **41**, 551.

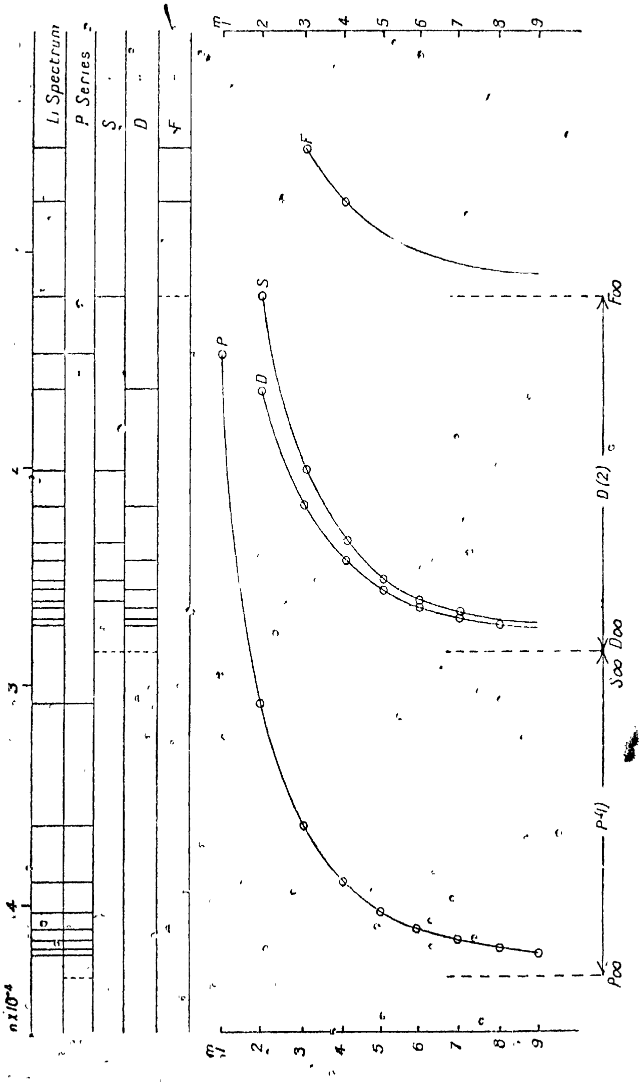

FIG. 73.—Series in the lithium spectrum.

When each component of a series is a *doublet* the series relationships are more involved. A P doublet series may be regarded as made up of two analogous single line series which converge to the same limit. Corresponding lines in these two part-series are said to form the components of a doublet, and the difference between the wave numbers of the components is termed the "interval" or vibration difference of the doublet. The intervals of the successive doublets in a P series converge towards zero as m increases. Associated with a P doublet series are D and S doublet series, but in these series the doublets do not close up but have a constant interval. The interval is the same for an S doublet as for a D doublet, and is further equal to the interval of the first P doublet. The data given in the accompanying table, referring to some of the doublets in the P, D, S series of rubidium, will serve to illustrate the preceding statements:—

RUBIDIUM SERIES LINES.

Principal Series n.	Diff.	Diffuse Series n.	Diff.	Sharp Series n.	Diff.
12,579 12,817	238	12,887 13,121	234	13,494 13,732	238
23,715 23,792	77	15,872 16,107	235	16,229 16,467	238
27,834 27,869	35	17 463 17,699	236	17,681 17,918	237
29,834 29,853	19	18,405 18,641	236	18 546 18,781	235
30,958 30,968	10	19,005 19,241	236	19,101 19,333	232

Doublets may be often recognised by the eye, but frequently the doublet intervals are so large that other spectrum lines come between the components of a doublet, which are thus difficult to find. It will be noticed that the D and S series for rubidium overlap in this manner.

Let the six single line series which together constitute the three associated P, D, S doublet series be denoted by $P_1, P_2, D_1, D_2, S_1, S_2$. Then $P_1\infty = P_2\infty$. The following relationships, strictly analogous to those already given for single series, are also found to hold good, viz. (i.) $D_1\infty = S_1\infty$ and $D_2\infty = S_2\infty$, (ii.) $P_1\infty - S_1\infty = P_1(1)$ and $P_2\infty - S_2\infty = P_2(1)$, and (iii.) $S_1(1) = -P_1(1)$ and $S_2(1) = -P_2(1)$. From these relationships it is easy to deduce that the six series equations, in the abbreviated notation of p. 235, become:—

$P_1(m) = 1s - mp_1$. More refrangible.
$P_2(m) = 1s - mp_2$. Less "
$D_1(m) = 1p_1 - md$. Less "
$D_2(m) = 1p_2 - md$. More "
$S_1(m) = 1p_1 - ms$. Less "
$S_2(m) = 1p_2 - ms$. More "

If, for a definite value of m, $S_1(m)$ is less than $S_2(m)$, it will be clear that $D_1(m)$ is also less than $D_2(m)$, but that $P_1(m)$ is greater than $P_2(m)$, *i.e.* the more refrangible components of the D and S doublets are associated with the less refrangible components of the P doublets, and *vice versa*.

The various relationships between the P, D, S *triplet* series are strictly analogous to those between P, D, S doublet series. The P series, for instance, is made up of three single line series which converge to a common limit. Corresponding lines constitute the components of a triplet, which is usually regarded as having two intervals, viz. that between the middle and the least refrangible line (ν_1) and that between the most refrangible and the middle line (ν_2). The values of ν_1 and ν_2 converge to zero as m increases. In the D and S triplet series the values of ν_1 and ν_2 are constants; ν_1 and ν_2 have, in general, different values, and, moreover, are equal to the intervals of the first P triplet. Further, the limits of $D_1(m)$, $D_2(m)$, $D_3(m)$, the part-series which together constitute $D(m)$, are respectively equal to the limits of $S_1(m)$, $S_2(m)$, $S_3(m)$, the part-series of $S(m)$; and so on.

A fourth type of series, the *Fundamental* or F series, may be mentioned. In the simplest case it is represented by the equation—

$$F(m) = N/(2+d)^2 - N/m^2, \quad m = 3, 4, \ldots,$$

and the relationship $D\infty - F\infty = D(2)$ is found to hold good.[1]

The lines belonging to one and the same series are similar in character.[2] Lines in different spectra (*i.e.* the spectra of different elements) that are similar in character and correspond to the same value of m in series of the same type are called *homologous* lines. In a similar manner it is possible to talk of homologous doublets, triplets, and series.

It has been mentioned that one series of lines, the Balmer series, has been found in the hydrogen spectrum; other series are also known in the same spectrum, and the same is true for the spectra of helium and neon. The spectra of the alkali metals sodium, potassium, rubidium, and cæsium contain P, D, and S doublet series, and it is very probable that what appear to be single line series in the lithium spectrum are really close doublet series. Aluminium, gallium, indium, thallium, and probably scandium, yttrium, lanthanum, gadolinium, and ytterbium show doublet series in their spectra. The spectra of magnesium, calcium, strontium, barium, radium, zinc, cadmium, mercury, and europium contain triplet series although all the P series are not yet known.

One of the most valuable methods for detecting homologous lines and series is to examine the influence of the magnetic field on the spectra. When a source of light which gives rise to a line spectrum is placed in a powerful magnetic field, many of the spectrum lines are found to be resolved into two, three, or even more, components, lying close together. This was discovered by Zeeman in 1896, and is called the *Zeeman effect*.[3] It is readily accounted for on the hypothesis that an atom consists of a central core surrounded by negative electrons, to the motions of which the spectrum lines of the element are due; for the motions of the electrons, which are electrically charged, would be affected by the magnetic field.

It was discovered by Preston[4] that, for the same magnetic field, all lines belonging to the same series exhibit exactly the same magnetic resolution when the results are expressed in wave numbers; and Runge and Paschen[1] found that this law could be extended to corresponding series for different elements. From the point of view of the Zeeman effect, it is necessary to consider a doublet (or triplet) series as being made up of two (or three) separate series, since the components of a doublet (or triplet) usually exhibit different types of resolution; in the case of helium, however, the types are all the same and of the simplest variety.[2]

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[1] For further details concerning F series, and for discussions of (i.) the "satellite" lines associated with certain D series and (ii.) the "combination" principle of Ritz, the references already given may be consulted.

[2] In observing the character of lines it is necessary to notice whether they are sharp or diffuse long or short, and readily self-reversed; how they are affected by the magnetic field, self-induction, etc. See Baly, *opus cit.*

[3] Zeeman, *Phil. Mag.*, 1897, [v.], **43**, 226; **44**, 55, 255; 1898, [v.], **45**, 197.

[4] Preston, *Sci. Trans. Roy. Dubl. Soc.*, 1899, [ii.], **7**, 7; *Phil. Mag.*, 1898, [v.], **45**, 325.

The first definite connection between the spectra of allied elements and their atomic weights was discovered by Lecoq de Boisbaudran,[3] who was thereby enabled to calculate the atomic weights of gallium and germanium by comparing their spectra with those of analogous elements. Better methods have since been devised. Rydberg[4] noticed that when the homologous series in the spectra of analogous elements (*e.g.*, K, Rb, Cs) were compared, the intervals of the doublets or triplets in the D and S series (or what are equivalent, viz. the intervals of the first P doublets or triplets) were nearly proportional to the squares of the atomic weights. For instance, comparing the D and S triplet series of cadmium and zinc, and using the notation already employed in this section, it is found that—

$$(\nu_1 + \nu_2)_{\mathrm{Cd}}/(\nu_1 + \nu_2)_{\mathrm{Zn}} = 2{\cdot}918$$

while

$$\mathrm{Cd}^2/\mathrm{Zn}^2 = 2{\cdot}960\,;$$

in other cases, however, the agreement is by no means as close.[5] Runge and Precht[6] assume that this proportionality is exact, provided that some other power of the atomic weight be taken, this power being approximately equal to two. Accordingly, they plot the logarithms of the atomic weights of analogous elements against the logarithms of the homologous doublet or triplet intervals and suppose that the points obtained lie on a series of straight lines, one for each series of analogous elements.

Runge and Precht applied their method to deduce the atomic weight of *radium* by comparing its spectrum with the spectra of magnesium, calcium, strontium and barium, and deduced the result Ra = 257·8. Ordinary chemical methods, however, show that the correct value for the atomic weight is 226.[7] The method of Runge and Precht is therefore inexact. The relationship between the logarithms of the atomic weights and of the frequency intervals is, in fact, not strictly linear; but an empirical connection may be deduced between them and expressed in an interpolation formula of the type:—

$$\text{log at. wt.} = a + b(\log \nu) + c(\log \nu)^2 + d(\log \nu)^3 + \ldots$$

When these equations are deduced for the various families of analogous elements it is possible by interpolation to obtain atomic weights with considerable accuracy. The deduction of atomic weights by extrapolation, however, is naturally less accurate, but nevertheless Watts has shown that by extrapolating the curve for Mg, Ca, Sr, and Ba a good value is obtained for the atomic weight of radium, viz. 226·6.[1]

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[1] Runge and Paschen, *Astrophys. J.*, 1902, **15**, 235, 333; **16**, 118, 123.

[2] See this volume, Part 2. For a full discussion of the Zeeman effect, see Zeeman, *Researches in Magneto-Optics* (Macmillan, 1913).

[3] Lecoq de Boisbaudran, *Compt. rend.*, 1869, **69**, 445, 606, 675, 694; 1870, **70**, 144, 974; 1886, **102**, 1291; see also Miss Freund, *Study of Chemical Composition* (Camb. Univ. Press, 1904), chap. xvi.; or Wurtz, *Dictionnaire de Chimie, Supplement*, p. 859; and *cf.* the criticism of Ames, *Phil. Mag.*, 1890, [v.], **30**, 33. Ames's paper contains an interesting account of the early work on the relations between the lines of various spectra.

[4] Rydberg, *loc. cit.*

[5] Marshall Watts, *Phil. Mag.*, 1903, [vi.], **5**, 203; 1904, [vi.], **8**, 279; *cf.* Runge, *ibid.*, 1903, [vi.], **6**, 698.

[6] Runge and Precht, *Phil. Mag.*, 1903, [vi.], **5**, 476.

[7] See Vol. III.

The uncertainty attaching to the preceding method is increased by Zeeman's observation that lithium does not fall into line with the other alkali metals.[2]

Another relationship between the wave numbers of certain homologous lines of analogous elements has been observed by Ramage, viz. that the differences between the wave numbers of the lines are proportional to the differences between the squares of the atomic weights of the elements.[3] For example, the following are homologous lines:—

	Ca.	(diff.)	Sr.	(diff.)	Ba.
n =	23,657·9		21,703·7		18,064·6
		(1954·2)		(3639·1)	

If, then, the atomic weights of calcium and barium are taken to be 40·1 and 137·4 respectively, and the value for strontium is denoted by x,

$$\{x^2-(40{\cdot}1)^2\}/\{(137{\cdot}4)^2-x^2\}=1954{\cdot}2/3639{\cdot}1,$$

whence $x=87{\cdot}42$, in good agreement with the experimental value.[4] The relationship thus illustrated is, however, only of limited application, *e.g.* in general it is not possible to choose the analogous elements so that some are in Mendeléeff's short periods and the others in the long periods (see Chap. VIII.).

The connection between the square of the atomic weight of an element and the doublet or triplet intervals of its D and S series has been further developed by Hicks.[5] Any of the series equations already mentioned may be written in the form

$$n=\mathrm{N}[1/\phi_1{}^2-1/\phi_m{}^2],$$

where $\mathrm{N}/\phi_1{}^2$ is the "limit" and $\phi_m=m+$ a fraction, the fraction being in general a function of the integer m. If this equation denotes the less refrangible components of a D or S doublet series, then, instead of representing the more refrangible components by the equation

$$n=\mathrm{N}[1/(\phi_1{}')^2-1/\phi_m{}'^2],$$

as was done, for instance, on p. 237, the alternative form, viz.—

$$n=\mathrm{N}[1/(\phi_1-\Delta)^2-1/\phi_m{}^2]$$

may be utilised. Similar equations may be written down for D and S triplet series, provided two different magnitudes Δ_1 and Δ_2 be employed. As the result of a critical examination of the line spectra of twenty-five elements, Hicks concludes that the magnitude Δ is, or the magnitudes Δ_1 and Δ_2 are, multiples of a quantity $(90{\cdot}4725\pm0{\cdot}013)\mathrm{W}^2.10^{-4}$, which is called by Hicks the *oun* and denoted by δ_1; W is the atomic weight of the element. Since the values of Δ, Δ_1, and Δ_2 are large multiples of the oun, it would appear at first sight that Hicks' results afford no evidence that the atomic weights utilised, *i.e.*, those at present in common use, are the correct multiples of their combining weights, but nevertheless certain numerical relationships are observed which enable the elements to be arranged in groups, and these groups are found to coincide with the sub groups of the Periodic Table (see Chap. VIII.); *e.g.* the values of $\Delta_1 + \Delta_2$ for Ca, Sr, Ba, Ra all appear to be multiples of $5\delta_1$, those for Zn, Cd, Hg are multiples of $6\delta_1$, etc. The most interesting feature of Hicks' work, however, from the chemical point of view, is that it suggests the possibility, when the requisite spectroscopic measurements have all been brought to a uniformly high degree of accuracy, of being able to calculate the atomic weights of the elements with an accuracy equal or superior to that which can be obtained by direct chemical synthesis or analysis.[1]

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[1] Marshall Watts, *Phil. Mag.*, 1904, [vi.], **8**, 279; 1909, [vi.], **18**, 411.

[2] Zeeman, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 155.

[3] Ramage, *Proc. Roy. Soc.*, 1902, **70**, 1, 303.

[4] Marshall Watts, *Phil. Mag.*, 1903, [vi.], **5**, 203; 1904, [vi.], **8**, 279; *cf.* Runge, *ibid.*, 1903, [vi.], **6**, 698.

[5] W. M. Hicks, *Proc. Roy. Soc.*, 1910, **A**, **83**, 226; 1912, **A**, **86**, 413; 1913, **A**, **89**, 125; *Phil. Trans.*, 1910, **A**, **210**, 57; 1912, **A**, **212**, 33; 1913, **A**, **213**, 323.

The various spectroscopic methods for deducing atomic weights, here outlined, were not developed until the modern atomic weight table had been firmly established, and few, if any, atomic weights were in doubt. Their applicability is therefore limited to elements that may be discovered in the future; but they obviously afford valuable corroborative evidence in favour of the atomic weights at present accepted. Similar remarks apply to Benoist's X-ray method (p. 234).

PRECAUTIONS TO BE OBSERVED DURING THE ACCURATE DETERMINATION OF ATOMIC WEIGHTS.[2]

With increasing knowledge of any science, there comes the demand for greater accuracy in the experimental work. Consequently the rough analyses with which chemists were satisfied fifty years ago have given place to more accurate determinations, and methods which were then regarded as satisfactory are now discarded as yielding too great an experimental error. In no sphere of science is this realised more acutely than in the one now under discussion. Whilst a century ago the atomic weights of many of the common elements were not known with certainty even to within one or two units, numerous investigators in recent times have spent years in determining them accurately to the second place of decimals; for example, it has now been definitely shown that the atomic weight of nitrogen is more correctly represented by the number 14·01 ($O = 16$) than by 14·04, which latter number was generally accepted until about the year 1905.

First among the steps which must be taken in the performance of any accurate atomic weight determination is the choice of methods to be used, involving the careful study of the nature of the substances which will best serve the purpose in view. Many an otherwise excellent piece of work has been rendered valueless by a wrong choice of material at the beginning; for often no amount of care can obtain significant results from unsuitable substances, and a bad method may nullify the value of many elaborate precautions.

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[1] For an attempt to express the constants in the Rydberg formulæ for analogous elements as functions of their atomic weights, see Ramage, *loc. cit.* Various attempts have been made to connect the spectra with the atomic volumes of the elements; see Hicks, *loc. cit.*; Halm, *loc. cit.*; Reinganum, *Physikal. Zeitsch.*, 1904, 5, 302; Rossi, *Phil. Mag.*, 1911, [vi.], **22**, 922.

[2] This and the succeeding section on the atomic weight of lithium are adapted and condensed from the excellent memoir by Theodore W. Richards, published by the Carnegie Institution of Washington, 1910, No. 125. The authors desire to acknowledge the courtesy and kindness of Professor Richards and of the President of the Carnegie Institution for permission to make full use of this memoir in the present work.

To make clearer the importance of careful forethought, it is worth while to emphasise some of the precautions which must be taken in choosing the best conditions in the determination of an atomic weight. Four main requirements must be fulfilled at the outset if the work is to have any value. In the first place, a compound must be selected which may be prepared in a perfectly pure state. Secondly, this compound must contain, besides the element to be studied, only elements with definitely known atomic weights. Thirdly, the condition of valency of the elements in this compound must be definite; thus, for example, an iron compound must be wholly ferrous or ferric. Fourthly, the compound selected must be capable of exact analysis, or else of exact synthesis from weighed quantities of the elements concerned.

All these four obvious requirements were perfectly clear to the early masters, Marignac and Stas, who endeavoured to work always in accordance with their demands. Their fulfilment, however, is not always easy, and it often requires wide chemical and physico-chemical knowledge to choose rightly the substance to be studied.

The material and methods having been chosen, the following work resolves itself into two parts: first, the qualitative task of the actual preparation of enough pure substance; secondly, the quantitative task of determining its composition, of comparing it with weighed amounts of other pure material, or of measuring some other special property under investigation.

Purity of materials is not always sufficiently sought. Even Stas, at times, with all his precautions, did not always attain a perfectly satisfactory result in this respect.

The quantitative process, which follows the qualitative purification, may consist either of chemical analysis or of physical measurement. Chemical analysis is, of course, very different from the qualitative preparation of the material, although in both cases the experimenter wishes to obtain, at the end of his experiment, a perfectly pure substance uncontaminated by any accidental impurities. The problem of the quantitative determination is vastly increased in difficulty by the fact that not only must the final substance be pure, but also every possible trace of that substance must be produced that can be produced. In the qualitative purification 90 per cent. of the substance may be lost without any anxiety; but in the quantitative estimation even the thousandth part of 1 per cent. must not be lost if it can be avoided; and if a minute percentage is lost, some process must be undertaken to prove its exact magnitude, so that due correction may be made. Physical measurement, whether of density, temperature, pressure, electromotive force, or any other property, is also entirely distinct from qualitative preparation.

Certain considerations apply to nearly all chemical work, whether qualitative or quantitative, since several physico-chemical tendencies of matter greatly affect the purity of nearly all preparations. The generality of these tendencies arise from the fact that materials are generally purified by changing the state or phase in which they exist. For example, a salt is purified by dissolving and crystallising it, taking it first into a liquid phase and then again bringing it back into the solid condition. A liquid is purified by distillation—a process involving a double change of phase. Thus the exact purification effected by any such process depends in each case upon what happens at the moment of formation of the new phase, as well as upon the completeness with which this phase may be separated mechanically from the residual one.

The complete separation of the substance concerned depends upon two different factors. Firstly, the phases must be separated completely from one another, otherwise each will be contaminated with the other and thus rendered impure. Solids, for example, must have adhering to them none of the liquid from which they were separated, and no liquid must be enclosed in cells within their substance. Liquids must retain none of a finely divided precipitate. Gases must be freed from fine drops or impalpable powder belonging to the phase from which they were to have been separated. This part of the separation is purely a mechanical one, involving the use of separating methods which depend, for their efficiency, upon the different properties and characteristics of the phases to be separated.

On the other hand, another more insidious cause of impurity exists in the tendency manifested by a phase to dissolve a portion from any other phase with which it may come into contact. This tendency manifests itself in solids as the so-called solid solution or isomorphous mixture; in liquids, as solubility; and in gases, as the vapour tension of the impurity. The contaminating substance retained in this fashion is not merely held in mechanical fashion, but becomes physico-chemically a part of the phase which contains it.

For example, the usual ways in which solids formed from liquids may be contaminated may be considered. The crudest and most obvious cause of contamination is purely mechanical; much liquid adheres to the surface of the solid. In the preparation of pure substances the centrifugal draining of the crystals is of enormous assistance in eliminating this adhering mother liquor. The advantages of centrifugal action, which has long been used in technical processes, have been appreciated by few scientific investigators.[1]

A less obvious, but merely mechanical, cause of incomplete separation, arises from the fact that all precipitates or crystals made from aqueous solutions contain included water which does not belong to them, even, for example, the beautifully brilliant and apparently quite dry crystals of electrolytic silver.[2] This appears to be very pure, but in reality contains both water and silver nitrate imprisoned in minute cells throughout its structure. Thus, as a rule, every solid prepared from a liquid which is to be weighed with accuracy should be fused in a dry atmosphere before weighing in order to expel the accidental water. Merely heating to 200° C. or more is not enough, because the traces of included liquid are not able to force their way out of the firmly knit solid structure.

Water may be held, not merely mechanically, but also in chemical fashion with great pertinacity. The presence of unsuspected traces of water constitutes one of the most insidious sources of error in precise chemical work. It is not easily found by chemical tests, and often produces no important change in the outward appearance of the substance in which it lurks, although its presence may be far more injurious than almost any other impurity. To illustrate this, suppose that the atomic weight of nickel is the constant to be determined, and that 0·1 per cent. of residual crystal water is present in nickel bromide to be analysed. This comparatively small amount of impurity would raise the resulting observed value for the atomic weight of nickel from 58·71 to 58·93, or more than a third of one per cent. The same amount of cobalt bromide present as an impurity would cause an error only about 1/700 so great, namely, about 0 0003—an amount wholly negligible.

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[1] The consistent use of this process has contributed much to the success of the Harvard work on atomic weights.

[2] Rayleigh and Sidgwick, *Phil. Trans.*, 1884, **175**, 470. Richards and his co-workers, *Proc. Amer. Acad.*, 1899, **35**, 123; 1902, **37**, 415. *Zeitsch. physikal. Chem.*, 1903, **46**, 189. *J. Amer. Chem. Soc*, 1915, **37**, 7. Hulett and his co-workers, *Trans. Amer. Electrochem. Soc.*, 1907, **12**, 257; 1912, **22**, 345.

The elimination of water is therefore one of the most important experimental problems presented to the exact analyst. This has been solved at Harvard by the gradual evolution of a very simple apparatus.[1] It consists of an ignition tube AB fitted into a soft glass tube CD which has a projection or pocket C in one side (see fig. 74). A weighing bottle is placed at the end of the latter tube, and its stopper in the pocket. The boat containing the substance to be dried is heated in the hard glass or quartz tube surrounded by an atmosphere consisting of any desired mixture of gases. These gases are displaced, after partial cooling, by pure, dry air, and the boat is pushed past the stopper into the weighing bottle by means of a wire through A, the stopper being then forced into place and the substance thus shut up in an entirely dry atmosphere. The weighing bottle may now be removed, placed in an ordinary desiccator, and weighed at leisure.[2]

In numerous cases it is impossible to fuse a substance without decomposition taking place. It is then necessary to dry the substance, preferably in the bottling apparatus already described, under definite conditions that may readily be reproduced, and to carry out special experiments in which the substance, dried as for an analysis, is decomposed in a suitable manner and the water set free collected in a phosphorus pentoxide tube and weighed.[3] In other cases it is possible to obtain a substance free from water by a suitable choice in the method of preparation. For instance, it is impossible to prepare anhydrous selenium dioxide by dehydrating selenious acid, but it can be accomplished by synthesising the oxide (which sublimes without melting) from selenium and oxygen.[4]

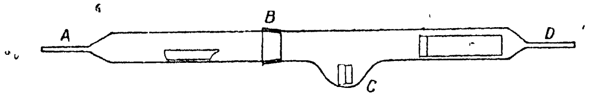

FIG. 74.

Still considering the pernicious influence of water, there exists one other class of substances to be mentioned—namely, substances which are decomposed by water. The problem in such cases is obviously not to eliminate water contained in the substances but to prevent access of water prior to the determination of their weight, and in general it is necessary to take particular precautions to purify the substances from the products formed from them by the action of water. The chlorides and bromides of the non-metals are cases in point.[1]

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[1] Richards, *Zeitsch. anorg. Chem.*, 1895, **8**, 267; Richards and Parker, *ibid.*, 1897, **13**, 86; Richards, Kothner, and Tiede, *J. Amer. Chem. Soc.*, 1909, **31**, 6; Richards and Willard, *ibid.*, 1910, **32** 4: *Carnegie Inst. Publications*, 1910, No. 125.

[2] See also Egan and Balke, *J. Amer. Chem. Soc.*, 1913, **35**, 365.

[3] Examples may be found in the work of Baxter and others; see Baxter and Coffin, *J. Amer. Chem. Soc.*, 1909, **31**, 297; Baxter and Jesse, *ibid.*, 1909, **31**, 541; Baxter, Mueller, and Hines, *ibid.*, 1909, **31**, 529; Baxter and Tilley, *ibid.*, 1909, **31**, 201; Baxter and Jones, *ibid.*, 1910, **32**, 298; Baxter and Chapin, *ibid.*, 1911, **33**, 1.

[4] Jannek and J. Meyer, *Zeitsch. Elektrochem.*, 1913, **19**, 833; *Zeitsch. anorg. Chem.*, 1913, **83**, 51.

The solvent itself is not, however, the only impurity carried down with the precipitate or crystal formed from a liquid; traces of any and all other substances which may be in solution are likewise adsorbed by the precipitate. Thus, in any ordinary metathetical precipitation the precipitate is likely to contain traces of all the acids and bases present, besides the components constituting the precipitate proper. Silver chloride, for example, when precipitated from sodium chloride by silver nitrate, may contain traces of sodium chloride, of silver nitrate, and of sodium nitrate, according to the manner of precipitation. The only way of guarding against this source of error is to use solutions at as great a dilution as possible. That portion of the adsorbed substance on or near the surface of the precipitate may usually be removed by thorough washing, but some is generally imprisoned beneath the surface, and no amount of washing can eliminate this. Those precipitates which, like silver chloride, have a loose sponge-like structure, may therefore be more successfully washed than the rigid crystalline ones; for the innermost pores of the spongy precipitates are accessible, while those of crystalline precipitates are not. Hence such precipitates are eminently suitable for precise work.

Not only do solids thus formed from liquids tend to hold the impurities which surrounded them at the moment of their formation, but solids formed from solids have precisely the same tendency. Thus cupric oxide made by the ignition of the basic nitrate always contains nitrogen, which is only eliminated at the temperature at which the oxide itself begins to decompose.[2]

The mechanical methods for removing solid impurities from liquids are so well known that attention need not be directed to them here, except, perhaps, to reiterate the advantages of centrifugal treatment and to emphasise in passing the convenience and accuracy of the Gooch-Munroe crucible, with a mat of polished platinum sponge as a filtering medium.[3] The physico-chemical causes of contamination of liquids, however, are less generally known. All liquids tend to dissolve a portion of every other phase, whether solid, liquid, or gas, with which they come into contact; *e.g.* the vessels in which the liquids are contained, the precipitates produced within them, and the gases above them. Sometimes the solubility is so slight as to be negligible; but more often than is generally supposed its extent is appreciable. Stas, who employed glass vessels, was never able to free his salts completely from silica. Increased accuracy is now attained in modern work by the use of vessels of platinum and fused quartz.

The solubility of precipitates affects the result of final quantitative analysis in obvious ways. If the precipitate is somewhat soluble in water, it will not all be collected upon the filter, and some means must be taken to estimate the amount which remains in solution. Moreover, if some of the precipitate dissolves, the end point of the reaction becomes difficult to detect, inasmuch as the dissolved portion is precipitated by addition of either of the ions to which it gives rise. Thus, a solution of silver chloride is precipitated by either a silver salt or a chloride.[1] In some cases Stas recognised this tendency, especially in his later work; but he did not always sufficiently heed it. He devised a simple instrument for estimating the traces of precipitate produced by adding suitable reagents to such very dilute solutions. This has been improved and made more general in its application, and has received the name of *nephelometer* or cloud measurer.[2] With this instrument minute traces of suspended matter may be estimated approximately from the brightness of the light reflected. The construction is very simple; two test-tubes, near together and slightly inclined to one another, are arranged so as to be partly or wholly shielded from a bright source of light by sliding shades. The tubes are observed from above through two thin prisms, which bring their images together and produce an appearance resembling that in the familiar half-shadow apparatus. The unknown quantity of dissolved substance is precipitated as a faint opalescence in one tube by means of suitable reagents; and a known amount treated in exactly the same way is prepared in the other. Each precipitate reflects the light, the tubes appearing faintly luminous. The amount in the second tube is adjusted until both tubes are exactly similar in appearance. The unknown quantity then admits of easy calculation.

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[1] For suitable methods of procedure, see Thorpe, *Trans. Chem. Soc.*, 1885, 47, 108, 129; Hoskyns-Abrahall, *ibid*, 1892, 61, 650; Gautier, *Ann. Chim. Phys.*, 1899, [vii.], 18, 352; Baxter, Moore, and Boylston, *J. Amer. Chem. Soc.*, 1912, 34, 259; Briscoe and Little, *Trans. Chem. Soc.*, 1914, 105, 1310.

[2] An appreciable part of the superiority of the more recent determinations of atomic weights over those of Stas and his contemporaries is due to the careful elimination of this type of error.

[3] C. E. Munroe, *J. Anal. Chem.*, 1888, 2, 241; *Chem. News*, 1885, 58, 101.

Liquids tend to dissolve not only solids, but also gases and other liquids. Consider, for instance, the final purification of silver. Stas undoubtedly contaminated his silver with oxygen by fusing it in an oxidising environment; and by suddenly cooling the silver by pouring it into water, he prevented this oxygen from escaping from the molten metal in the act of solidifying. The error of 0·05 per cent. in his value for the atomic weight of chlorine is to be traced at least in part to this source, for he assumed that his silver was pure, and that the gain in weight on conversion into the chloride represented all the chlorine added.[3] This particular difficulty has only been overcome by rigorously excluding all oxygen and fusing silver either in vacuum or in hydrogen. Not only solids and liquids have this tendency of holding back other substances taken from the phases around them; gases may also carry away, both mechanically and physico-chemically, portions of the phases with which they are associated. Gases evolved from solids often carry away fine powder with them, particularly in cases where the decomposition of the solid involves considerable molecular rearrangement. It seems as if the molecule, in its upheaval, is separated from its fellows, and hence an impalpable powder of almost molecular fineness may be carried away with the evolved gas. Gases from liquids also, provided they escape in the form of bubbles, always carry for a long distance exceedingly fine drops which result from the bursting of these bubbles on the liquid surface On the other hand, there is good evidence that the drops are not mechanically carried away to an appreciable extent when the evaporation is conducted without the formation of bubbles, and accordingly quantitative evaporation should be carried out either on the steam bath or in a vacuum desiccator or with the help of a downward blast of pure air at a temperature just below the boiling-point.[1] The first-named of these processes cannot be used in the most exact work because it contaminates the substance with the impurity almost inevitably present in the air of the laboratory.

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[1] Mulder, *Silberprobi. Methode*, 1859; Richards and Wells, *Carnegie Institution of Washington*, 1905, Publication **28**, pp. 24, 45.

[2] Richards, *Zeitsch. anorg. Chem.*, 1895, **8**, 269; Richards and Wells, *Amer. Chem. J.*, 1904, **31**, 235; Richards, *ibid.*, 1906, **35**, 510. See also Kober, *J. Amer. Chem. Soc.*, 1913, **35**, 1585; Briscoe and Little, *loc. cit.*

[3] Richards and Wells, *Carnegie Institution of Washington*, 1905, Publication **28**, p. 2.

Evaporation or distillation under diminished pressure is especially to be recommended if carried out with suitable precautions. The considerable lowering of the temperature of evaporation diminishes the risk of decomposition of a somewhat unstable substance, and greatly decreases the effect of all the solvents and vapours upon the vapours employed. As a general rule, the lower the pressure the more advantageous the process, and for an obvious reason. If any air still exists in the apparatus, the vapour of the liquid to be evaporated may go from the solution to the condenser or to the absorbing material in the desiccator only by pushing this air aside. Passage from the solution to the drying material is thus effected by the slow process of diffusion. On the other hand, when all the air is removed, no impediment exists in the passage of the vapour from one place to the other. As the vapour is condensed or absorbed, a partial vacuum is created which is immediately replenished from the liquid to be evaporated, and the process proceeds with great rapidity.

Physico-chemically, gases may carry away impurities by evaporation, as is well known. Possible loss of material in this way must always be guarded against. Precaution must also be taken to guard against possible introduction of impurity from incoming gas, which may be contaminated with volatile impurities taken from so-called purifying agents or improperly used rubber tubes. For example, it is frequently recommended to purify hydrogen by passing it through potassium permanganate, silver nitrate, strong sulphuric acid, and calcium chloride one after the other. The potassium permanganate contaminates the hydrogen with traces of oxygen; the silver nitrate is partly reduced by the light of the laboratory, and adds an impurity of an oxide of nitrogen; the sulphuric acid fails to remove these impurities, and adds sulphur dioxide because of its own reduction by hydrogen; the calcium chloride, not being so good a desiccating agent as sulphuric acid, adds water vapour to the list of contaminating substances. Thus the hydrogen emerges from the train of so-called purifiers distinctly less pure than it was in the first place.[2]

The construction of the laboratory is by no means unimportant in carrying out precise quantitative work. The ideal laboratory should be built as the modern hospital is built, and every precaution taken against dust and fumes. Nevertheless, even in a badly arranged laboratory excellent work may be done if precaution is taken to carry out all the manipulations under cover, protected from dust and noxious vapours. The laboratory is important, but is by no means the most essential condition for the performance of accurate work.

Having dealt with the various possible sources of contamination of materials, the quantitative side of the matter may now be discussed. Measuring apparatus of various kinds must here be used. The apparatus must be good, of course, but extraordinary refinement or outward beauty is not always necessary. As a rule, physical errors are more easy to avoid than chemical ones, as is shown by the fact that physical data are usually known to a much higher degree of percentage accuracy than chemical data. The difference in precision is by no means due to greater intelligence and care on the one side of the two classes of scientific men than on the other, but rather to the nature of the two problems concerned.

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[1] See Richards and Forbes, *Carnegie Institution of Washington*, 1907, Publication 69, p. 53.

[2] Similar instances are by no means uncommonly recounted in the literature, and often they have led to the complete nullification of any usefulness which might otherwise have existed in the final results of an investigation.

A comparatively simple piece of apparatus of known error and capable of accurate correction is better than a complex contrivance of unknown error, provided that in essentials the apparatus is adequate.

The quantitative operation most frequently employed is that of weighing. For this purpose any good balance will serve, provided it yields constant results. The errors in weighing usually arise from the changing buoyancy of the air and the variation in the hygroscopic and electrical condition of the surface of the vessels weighed. These errors cannot be cured by the most expensive and sensitive balance, but must be intelligently eliminated with the greatest care. The admirable work of Landolt[1] exemplifies this fact in a striking manner. Weighing should be effected by substitution, using, both as makeweight and as tare, vessels precisely similar in volume, weight, and surface to the vessel containing the substance to be weighed. The rôle played by the balance itself is nearly always the most accurate part of the whole process if the weights have been properly standardised.

A word about the scale of operations is perhaps not out of place. Shall the experimenters use a very large quantity of material as Stas did, or shall he adopt an infinitesimal quantity as is recommended by Hinrichs? The answer to this question varies somewhat according to the circumstances of the particular case. When a small amount of impurity is to be estimated in a substance, much material should be used in analysis, as everyone knows. This is not always so true, on the other hand, when the whole amount of substance is to be precipitated instead of merely a very small fraction of it. In this latter case the accuracy of the work depends more on the purity of the original material and of the precipitate, and upon the completeness of the reaction, than upon the quantity of material used in the individual experiments.

For example, Stas used very large quantities of material, sometimes as much as 400 grams of silver in a single experiment, hoping in this way to increase the accuracy of his results. Obviously, however, since the purely chemical errors and not the errors of weighing formed the largest part of the cause of uncertainty in the outcome, this expenditure of time was often misplaced. To obtain a precision of one part in 100,000, it is only necessary to weigh 400 grams to within 4 milligrams. If the silver contains as much as one-thousandth of 1 per cent. impurity, there is no use in weighing it more accurately than this. Now Stas's silver probably contained at least fifteen times this percentage of impurity. Evidently, then, if he had weighed his 400 grams of silver to within 6 centigrams, it would have been as accurately weighed as the purity of his material warranted. Ten grams of silver weighed to within one milligram (a degree of accuracy attainable in any analytical balance) would have yielded just as good results as those he actually obtained. The enormous expenditure of time put upon these large quantities of material was therefore wasted; it would have been much better if it had been spent in making the silver really pure in the first place.

In most of the modern Harvard work upon atomic weights a greater degree of accuracy than one part in 100,000 was not attempted, 10 grams of material being usually sufficient to use in any experiment to enable this accuracy to be realised. The effort should be made, therefore, not to spend needless exertion in preparing enormous quantities, but rather to put time and energy into making the substances actually weighed really pure, so that 10 grams shall consist of nothing but that which it is supposed to be.

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[1] Landolt, *Abhandlungen der Bunsen Gesellschaft*, 1909, No. 1; and the references quoted on p 5.

It is true that with large quantities, other things being equal, a somewhat higher degree of mechanical accuracy can be attained, but this, in many cases, is undoubtedly offset by the extraordinary difficulty of preparing a very large amount of any substance in a state of the highest purity. On the other hand, the use of very small amounts of material in analytical work unquestionably leads to equally great errors from another cause. Here it is easy to purify substances, but because of the limitations of sight and manual dexterity it is not possible to analyse them accurately. If only 1 gram of material is taken, for example, one must collect and weigh one's precipitate to within the hundredth of a milligram in order to attain an accuracy of one part in 100,000—and this is practically impossible. Hence common sense dictates the choice of a middle path between the two extremes, using quantities of material not less than 5 grams or over 50 grams if a degree of accuracy such as that mentioned above is desired. With 5 grams this degree would be attained by weighing to within one-twentieth of a milligram—a degree of precision perfectly attainable as regards both the collecting of the precipitate and the process of weighing.

The best apparatus and the best methods possess faults, and these must be evaluated and corrected before a precise result is to be obtained. The methods of doing this vary so much with the details of the special processes that only one or two general remarks can be made here. It may be taken as a general precaution that control experiments should always be performed under precisely the same conditions as govern the main experiment. Suppose, for example, that a substance is to be evaporated and weighed in a quartz flask. The weighing must be done by comparison with a counterpoise flask filled with dry air at the same temperature, cooled in the same fashion as the flask containing the precious material. The weighing must be done by substitution, and during the process each flask must be treated in precisely the same way in order that any errors pertaining to one weight shall accrue likewise to the other. Thus in a sense the empty counterpoise flask is a control.

ACCURATE DETERMINATIONS OF ATOMIC WEIGHTS.

In the previous section attention has been drawn to the extreme care required in modern determinations of atomic weights. In order to further exemplify this and to illustrate the general method of procedure, two typical examples will now be described—namely, the revision of the atomic weight of lithium by Richards and Willard, and that of nitrogen by Guye and his collaborators.

The former is essentially a chemical investigation, comprising a number of careful gravimetric analyses of lithium chloride; it is typical of many excellent atomic weight determinations effected by the analysis of a chloride or bromide. The latter is partly a chemical and partly a physical research. The chemical methods are noteworthy owing to their unusual character, and also because they afford the required atomic weight by direct reference to oxygen; the physical methods are interesting, since the results they afford, although less accurate and conclusive than those obtained chemically, nevertheless confirm the chemical value in a very satisfactory manner.

1. THE ATOMIC WEIGHT OF LITHIUM.

During the early part of the nineteenth century no fewer than twelve different investigators made separate and independent determinations of the atomic of lithium, but their results were far from concordant, ranging from 6·1 (Hermann, 1829) to 10·1 (Arfvedson, 1817).[1] In 1865 Stas[2] determined the ratios LiCl/Ag and $LiCl/LiNO_3$, and found the corresponding atomic weights of lithium to be 7·003 and 6·96 respectively, when that of silver is taken as 107·88. The difference between these two values amounts to practically 1 per cent.—a result that cannot be considered satisfactory, and that is, moreover, very remarkable in view of the high degree of accuracy usually attained by Stas in his investigations. Twenty-four years later Dittmar[3] determined the ratio Li_2CO_3/CO_2 and found the atomic weight of lithium to be 6·89 (Ag = 107·88), a result which does not agree with either of those obtained by Stas. This was the state of our knowledge when Richards and Willard[4] began their investigations, and, by studying the ratio LiCl/AgCl,[5] showed that the correct atomic weight of lithium is 6·94. Their method of procedure was as follows:—

The Preparation of Materials.—All the materials used in the research were purified with the greatest care. The most insidious sources of impurity in work of this kind are dust and the various gases sometimes contained in the air of the laboratory, and the most efficient methods of purification may fail to give a pure product unless careful attention is paid to this. The presence of dust, which always contains sodium, was especially noticeable in the preparation of pure lithium salts where sodium was the element most difficult to remove. It was found that a lithium salt free from sodium always acquired traces of this element after being crystallised in the usual way. The air of the room was therefore kept as pure as possible, and all evaporation and handling of solutions and salts in the final work were conducted in a large glass case. All heating was conducted electrically in order to avoid the deleterious effects of products of combustion. The vessels used in purifying materials were usually of quartz or platinum. Where glass was unavoidable, the best Jena glass was employed.

Water.—Distilled water of the laboratory was twice redistilled, once from alkaline permanganate and once alone using pure tin condensers without rubber or cork connections. In special cases the water was condensed and collected wholly in platinum. Dust was excluded by passing the end of the condenser through a hole blown in the bulb of a small flask which rested on the mouth of a large Jena flask in which the water was collected and stored. Water was always distilled just before use.

Nitric Acid.—Carefully tested pure nitric acid of commerce was redistilled, using a platinum condenser. When required to be free from chlorine the first portion was rejected and the acid redistilled until it showed no trace of this element with the nephelometer.

Hydrochloric Acid.—The pure acid of commerce was boiled with a little pure potassium permanganate and then repeatedly distilled, using a quartz condenser.

Ammonium Fluoride.—Pure hydrofluoric acid was distilled in a platinum t and neutralised by distilling into it pure ammonia obtained from concentrated solution.

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[1] For full references to these researches see Vol. II. of this series.

[2] Stas, *Œuvres complètes*, i. 710 and 717.

[3] Dittmar, *Proc. Roy. Soc. Edin.* 1889, 35, ii. 429.

[4] Richards and Willard, *Carnegie Institution of Washington*, 1910, Publication 125.

[5] The ratios LiCl/Ag and $LiClO_4/LiCl$ were also studied.

Hydrazine Hydrate.—This was prepared by distilling to dryness in platinum vessel a mixture of hydrazine sulphate and twice the theoretically requisite quantity of potassium hydroxide solution. The distillate was redistilled to free it from the traces of alkali carried over in the first operation, and preserved in a platinum vessel.

Silver.—This metal was prepared by several different modifications of the following method. Pure silver nitrate was recrystallised five times from dilute nitric acid, the crystals being centrifugally drained in platinum funnels. The silver was then precipitated by ammonium formate (prepared from redistilled ammonia and formic acid) and fused on pure lime in a current of hydrogen.

Lithium Chloride.—The most common impurities in lithium salts, and likewise the most difficult to eliminate, are compounds of the alkali and alkaline earth metals. In the material forming the source of the lithium chloride in the work the only appreciable impurities were iron, calcium, potassium, and sodium, as well as, possibly, traces of magnesium. It is true that none of the last-named metal was ever detected, but Richards and Willard rightly argue that this does not prove its entire absence owing to the lack of a sufficiently delicate reaction for the same. Since iron can be easily removed, the separation of potassium, sodium, calcium, and magnesium required the most careful consideration, the relative effects on the atomic weight of lithium varying in the order given, that of the potassium being greatest.

Attention was first turned to the methods of eliminating potassium and sodium, which go together. Those employed by previous investigators were either inadequate or extremely wasteful. A study was therefore made of the most suitable salts for the purpose. A search among the insoluble salts of lithium showed that the solubility of the fluoride is only 2·7 grams per litre, whereas sodium fluoride is 16 times and potassium fluoride 340 times more soluble. It was further found that the solubility of lithium fluoride is not appreciably affected by the presence of ammonium salts. Evidently the precipitation of lithium fluoride by ammonium fluoride ought to be an extremely efficient means of removing potassium and sodium without appreciable loss of lithium, and this was found to be true.

But this method does not remove calcium and magnesium, since their fluorides are even less soluble than lithium fluoride. These may be wholly separated, however, by recrystallisation of the lithium as the perchlorate or nitrate. Hence the following method of purification was ultimately adopted. The fluoride, free from sodium and potassium, but containing possible traces of calcium, magnesium, and sulphate, was converted into nitrate by heating in a platinum retort with nitric acid. The product was recrystallised several times, using centrifugal drainage.

Since even in the mother liquors from the first recrystallisation no calcium, magnesium, or sulphate could be detected by ordinary tests, there is no doubt that the recrystallised salt was exceedingly pure. All silica must have been removed when the fluoride was dissolved in acid.

The final step of the sequence of operations alone remained to be taken, namely, the conversion of the salt into lithium chloride. The solution was poured into a hot concentrated solution of ammonium carbonate which had been distilled in a platinum retort, and the precipitated lithium carbonate was washed several times with hot water, using centrifugal drainage. It was essential that hot and concentrated solutions should be used; otherwise the yield of carbonate was small. The precipitate was coarsely crystalline and easily washed. This process obviously served as a further means of purification and rendered certain the elimination of any traces of fluoride which might have found its way through the successive recrystallisations of the nitrate. The carbonate was dried at 300° C., dissolved in slightly less than the theoretical amount of the purest hydrochloric acid which had been twice distilled, condensed, and collected in quartz vessels. The solution contained a trace of nitrate, and to convert this into chloride without fear of attacking the platinum, a solution of hydrazine hydrate (see p. 251) was added, and then excess of hydrochloric acid. After boiling the liquid for a few minutes, all the nitrate was reduced, and there remained a solution of pure lithium chloride with a little hydrochloric acid and hydrazine chloride, both of which were completely volatilised in subsequent operations. The chloride was crystallised once or twice and dried as indicated below. It was then ready for analysis.

Drying and Weighing the Lithium Chloride.—The final preparation of the salt for analysis consisted in expelling the last traces of water by fusion in a platinum boat in a current of dry hydrochloric acid gas and nitrogen. To this end the apparatus shown in fig. 74 (p. 244) was employed. The gases issued under slight pressure, and the temperature was slowly raised so as to expel from the salt as much water as possible before fusion. The chloride was maintained in a state of fusion at red heat from 15 to 20 minutes in an atmosphere of hydrogen chloride, which latter was then replaced by pure nitrogen and the lithium chloride allowed to cool. It was then quite transparent and colourless. Inasmuch as fused sodium chloride is essentially free from dissolved nitrogen when prepared under analogous conditions,[1] it seems reasonable to assume that the lithium salt likewise contained no appreciable quantity. After the nitrogen had been displaced by dry air, the boat was bottled and placed in a desiccator. The platinum boat was always weighed separately before and after the operation, but the loss in weight was only a few hundredths of a milligram—sometimes none at all. The weighings were conducted with a Troemner balance, and successive weighings of the same object were rarely found to differ by more than 0·02 mg. The Sartorius gold-plated brass weights and rider were standardised from time to time by the method described by Richards,[2] and all weighings were made by substitution, using a counterpoise similar to the object being weighed. The weights required were, in consequence, never large in amount, and the influence of changes in atmospheric conditions was negligible. The vacuum corrections applied were as follows, the density of the weights being 8·3 :—

	Density	Vacuum Correction per Gram.
Silver	10·49	−0·000030
Silver chloride . . .	5·56	+0·0000732
Lithium chloride[3]	2·068	+0·000436
Lithium perchlorate	2·428	+0·000350

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[1] Richards and Wells, *J. Amer. Chem. Soc.*, 1905, **27**, 513.

[2] Richards, *J. Amer. Chem. Soc.*, 1900, **22**, 144.

[3] Baxter, *Amer. Chem. J.*, 1904, **31**, 558.

After weighing, the platinum boat containing the fused chloride was placed in a 3-litre Erlenmeyer flask of Jena glass, fitted with a ground and polished stopper. 50 to 80 c.c. of water were now added, and when the chloride had dissolved, and a drop of phenolphthalein coloured faintly pink with a trace of sodium hydroxide had proved the solution to be entirely free from any trace of acid, about one litre of water was added, the platinum boat removed and washed, the washings being added to the contents of the flask.

Precipitating and Weighing the Silver Chloride.—The precipitation of the silver chloride and all subsequent operations were carried out under red light in the dark room. To the solution of lithium chloride was added exactly the calculated amount of silver dissolved in a moderate excess of nitric acid, the concentration being approximately decinormal. The mixture was shaken for ten minutes and allowed to stand overnight. The next day it was again shaken, and to it was added the excess of silver nitrate required for complete precipitation—about 0·05 gram of silver per litre. This method greatly diminishes the danger of occlusion of silver nitrate.[1] The solution was shaken from time to time during the next day, and after standing until the supernatant liquid was perfectly clear, it was ready for filtration.

In the final experiments a Gooch-Munroe crucible[2] was used. The complete removal of silver chloride from the platinum sponge, when preparing for a new analysis, required treatment with concentrated ammonia for at least 12 hours, followed by a very thorough washing. The crucible was always dried overnight at 250° C. and a perforated platinum plate was placed upon the sponge to prevent rupture by the contraction of the silver chloride as it dried. The clear solution was poured through the crucible and the precipitate washed four times by decantation with a cold acid solution of silver nitrate, about two-hundredth normal. The filtrate and washings were always practically free from excess of chlorine, so that a constant correction of 0·04 mg. of silver chloride per litre was applied to them.[3] The precipitate was then washed ten times with very dilute nitric acid previously cooled in ice to reduce the solubility of the silver chloride, and finally transferred to the crucible by means of a jet of pure, cold water from a hydrostatic wash bottle. The entire process was conducted under a clean pane of glass to prevent dust from falling into the crucible. The latter was finally wiped with a clean cloth and heated in the electric oven, gradually increasing the temperature to 250° C., where it was maintained for at least 10 hours. After it had been weighed, the main mass of silver chloride was separated from the platinum disc and fused in a covered quartz crucible contained in a larger one of porcelain. Since the cover was transparent, it was possible to free the fused chloride from the bubbles which invariably adhered to the crucible, without danger of loss from spattering, by carefully rotating the crucible. With one or two exceptions the fused silver chloride was perfectly colourless and transparent, showing the absence of organic dust and occluded silver nitrate. The loss on fusion was very small, never more than a few hundredths of a milligram per gram; the correction for the entire weight of silver chloride was calculated from that of the portion fused—always over 90 per cent. of the total.

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[1] Richards and Staehler, *J. Amer. Chem. Soc.*, 1907, 29, 632.

[2] Snelling, *J. Amer. Chem. Soc.*, 1909, 31, 456. Munroe, *J. Anal. Chem.*, 1888, 2, 241; *Chem. News*, 1885, 58, 101.

[3] Richards and Wells, *J. Amer. Chem. Soc.*, 1905, 27, 487, 517.

The flask, in which the original precipitation was carried out, was rinsed with ammonia to remove any chloride that might have escaped observation. This, with the washings, was tested as follows: To the total washings, exclusive of those with dilute silver nitrate, was added 0·07 gram of silver as nitrate and, after the opalescence had appeared, it was dissolved by pouring into the ammoniacal rinsings. The volume was then made up to one litre. A standard solution was prepared containing in one litre a known amount of chloride and the same quantity of ammonia and silver as present in the washings. 25 c.c. of each were now pipetted into nephelometer tubes (see p. 246), 2 c.c. of dilute nitric acid added to each, and the contents stirred. The tubes were covered with glass caps each having a plane top and allowed to stand for 3 to 5 hours until constancy was attained. By the use of ice-cold wash-water the total nephelometer correction was reduced to about 0·35 mg. In the following table are given the results of the final series of experiments, from which it is evident that the atomic weight of lithium is 6·940, when the atomic weights of silver and chlorine are taken as 107·880 and 35·457 respectively.

THE ATOMIC WEIGHT OF LITHIUM.

Weight of Fused LiCl (Vacuum).	Weight of Fused AgCl (Vacuum)	$\frac{LiCl}{AgCl}$	Atomic Weight of Lithium. Ag = 107·880 Cl = 35·457.
6·28662	21·25442	0·295779	6·9391
5·82076	19·67873	0·295790	6·9407
6·70863	22·68030	0·295791	6·9409
6·24717	21·12073	0·295784	6·9399
5·50051	18·59600	0·295790	6·9407
8·34521	28·21438	0·295779	6·9391
6·65987	22·51564	0·295789	6·9406
45·56877	154·06020	0·295786	6·9401

2. THE ATOMIC WEIGHT OF NITROGEN.

The researches on the atomic weight of nitrogen, carried out at Geneva since 1904 by P. A. Guye and his collaborators,[1] include the analysis of nitrous oxide, both gravimetrically[2] and volumetrically,[3] the gravimetric analyses of nitrosyl chloride[4] and nitrogen peroxide,[5] the indirect volumetric analysis of ammonia,[6] the determination of the densities of nitrous oxide and ammonia[1] by the volumetric method, and the density of nitric oxide by the ordinary globe method,[2] and, finally, the measurement of various gaseou compressibilities[3] and critical constants.[4]

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[1] A detailed account of the physical measurements carried out in connection with this work is given by Guye in "Recherches expérimentales sur les propriétés physico-chimiques de quelques gaz en relation avec les travaux de révision du poids atomique de l'azote" (Guye, *Mém. Sci. phys. nat.*, 1908, **35**, 548–694).

[2] Guye and Bogdan, *J. Chim. phys.*, 1905, **3**, 537; *Compt. rend.*, 1904, **138**, 1494.

[3] Jaquerod and Bogdan, *J. Chim. phys.*, 1905, **3**, 562; *Compt. rend.*, 1904, **139**, 94.

[4] Guye and Fluss, *J. Chim. phys.*, 1908, **6**, 732.

[5] Guye and Drouginine, *J. Chim. phys.*, 1910, **8**, 473.

[6] Guye and Pintza, *Mém. Sci. phys. nat.*, 1908, **35**, 594.

It may be stated here that all pieces of apparatus were weighed by the method of vibrations against counterpoises of similar material and shape, and of nearly equal weight, and all weighings corrected to the vacuum standard.

Preparation and Purification of Nitrogen Compounds Used.—

Nitrous oxide.—Since the gas, prepared by any of the usual methods, is always slightly contaminated with nitrogen, recourse was had to the method devised by V. Meyer.[5] Concentrated sodium nitrite solution was dropped from the vessel D (fig. 77, p. 261) into a neutral solution of hydroxylamine sulphate contained in the flask E. The gas evolved was passed through potassium hydroxide solution and concentrated sulphuric acid in the bottles N and P respectively, and finally dried with phosphoric anhydride in S. The solutions were prepared in air-free distilled water, and at the commencement of each experiment the apparatus was evacuated through the tube F; a small quantity of gas was then disengaged, and the apparatus again exhausted. A repetition of this procedure once or twice served to completely eliminate last traces of air, when the tube F was sealed.

Nitric oxide.—This gas was produced by three distinct methods, namely: (*a*) Nitric acid (25 per cent.) was allowed to flow, drop by drop, into a boiling concentrated solution of ferrous sulphate in dilute sulphuric acid, or a concentrated solution of sodium nitrite was slowly added to one of ferrous chloride in hydrochloric acid.[6] The evolved gas (20 litres) was collected over air-free water in a copper gas-holder, from which it was afterwards driven through concentrated sulphuric acid and over phosphoric anhydride, and the dry gas condensed in a receiver cooled in liquid air. (*b*) A 2 per cent. solution of sodium nitrite in concentrated sulphuric acid was run into an Erlenmeyer flask, the bottom of which was covered with a layer of mercury.[7] The nitric oxide produced was led through concentrated sulphuric acid, and then condensed at the temperature of liquid air. Air was initially eliminated from the apparatus by a process similar to that described under nitrous oxide. (*c*) A 10 per cent. solution of sulphuric acid was added, drop by drop, to aqueous sodium nitrite (6 per cent.). Nitric oxide is produced in this reaction by auto-oxidation of the nitrous acid initially formed:—

$$3HNO_2 = HNO_3 + 2NO + H_2O.$$

The gas was thoroughly dried by conducting it through three vessels containing sulphuric acid, and finally liquefied.

It will be noted that higher oxides of nitrogen were always absorbed by concentrated sulphuric acid, and not by potassium hydroxide, since the latter reagent slowly decomposes nitric oxide, producing potassium nitrite and nitrous oxide.

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[1] Guye and Pintza, *Compt. rend.*, 1904, 139, 679; 1905, 141, 51; "Recherches expérimentales," *loc. cit.*

[2] Guye and Davila, *Compt. rend.*, 1905, 141, 826; "Recherches expérimentales," *loc. cit.*

[3] Jaquerod and Scheuer, *Compt. rend.*, 1905, 140, 1384; "Recherches expérimentales," *loc. cit.*

[4] Jaquerod, *Ber.*, 1906, 39, 1451; Briner, *J. Chim. phys.*, 1906, 4, 479; "Recherches expérimentales," *loc. cit.*

[5] V. Meyer, *Annalen*, 1875, 175, 141; Treadwell, *Anal. Chemie*, 1902, vol. ii. p. 512; also Treadwell-Hall, *Analytical Chemistry* (Wiley & Sons).

[6] Gay-Lussac, *Ann. Chim. Phys.*, 1843, (iii.), 23, 203; Thiele, *Annalen*, 1889, 253, 246. Emich, *Monatsh.*, 1892, 13, 73.

The impurities still present in nitric oxide, prepared by the above methods, include small quantities of nitrous oxide and nitrogen, and traces of higher oxides of nitrogen, and such substances as hydrochloric acid, sulphur dioxide, and chlorine derived from the reagents used. A consideration of the boiling-points of the impurities suggested that it should be possible to prepare nitric oxide free from all these impurities with the possible exception of nitrogen, by liquefaction and fractional distillation. The presence of even 0·15 per cent. of nitrogen, however, would only cause an error of 0·01 per cent. in the value for the density of the gas. Accordingly, the nitric oxide was liquefied, and boiled under reduced pressure, whereby the more volatile portions escaped, and the residue solidified. It was again liquefied, the more volatile portion again boiled off, and the procedure repeated five or six times, until the volume of the liquid had been reduced by one-half. The solidified residue was then slowly sublimed, under reduced pressure, and the final third rejected. This fractional sublimation was repeated in various experiments from two to five times.

Nitrogen Peroxide.—This was prepared by mixing, at - 20°, purified and carefully dried nitric oxide with excess of pure oxygen, prepared from potassium chlorate. The nitrogen peroxide was repeatedly distilled under reduced pressure in the presence of oxygen, to ensure the absence of trioxide, which would have been difficult to remove by distillation. Special precautions were taken to free the final product from dissolved oxygen

Although nitrogen peroxide decomposes into nitric oxide and oxygen at moderately high temperatures, at ordinary temperatures the extent to which this decomposition proceeds is quite insignificant, and the peroxide may therefore be regarded as a stable substance.

Ammonia.—Ammonia prepared from commercial ammonium salts is always contaminated with traces of organic bases such as pyridine, which materially raise its density. Accordingly, the gas obtained from a cylinder containing 20 kilograms of liquid ammonia (the first half collected in the distillation of a supply of commercial liquid ammonia) was slowly passed through a long, hard glass tube packed with little pieces of lime and heated to redness. The organic compounds were thereby decomposed, the nitrogen contained in them being converted into ammonia. The resulting ammonia was collected in pure hydrochloric acid solution, and on crystallisation pure ammonium chloride was obtained.

The apparatus for obtaining pure, dry ammonia for density measurements consisted of a large cylindrical tube, filled with a mixture of pure ammonium chloride and quicklime, and connected with a purifying and drying system of six tubes. The first three of these were filled with solid potassium hydroxide; the others contained anhydrous barium oxide. All the connections were of glass. The apparatus was initially evacuated, and then swept out once or twice with dry ammonia, liberated at a convenient rate by suitably warming the mixture of ammonium chloride and lime.

Nitrosyl Chloride.—This substance was prepared by Tilden's method,[1] a mixture of nitrosyl hydrogen sulphate and sodium chloride in equivalent quantities being warmed *in vacuo* in a small flask to 85° C. The distillate was collected in a small receiver cooled in a bath of solid carbon dioxide and ether. The materials were previously dried in a vacuum over phosphoric anhydride, and the apparatus thoroughly desiccated, since nitrosyl chloride is immediately decomposed by water. For the purification, the nitrosyl chloride was several times fractionally crystallised, the final crystals melted, and the liquid submitted to fractional distillation, with the rejection each time of the first and last fractions. The impurities thus eliminated included traces of hydrogen chloride, chlorine, sulphur dioxide, and higher oxides of nitrogen.

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[1] Tilden, *Trans. Chem. Soc.*, 1860, **12**, 630, 852.

Analytical Methods:—(*a*) *Gravimetric Analyses.*—In the cases of nitrous oxide and nitrogen peroxide, weighed quantities of the compounds were decomposed by red-hot iron, which quantitatively absorbed the oxygen. Iron spirals were employed, wound on thin porcelain rods, and electrically heated. After an experiment, a spiral was prepared for further use by being heated in a current of pure hydrogen. Since each spiral used was oxidised and reduced a number of times in succession before the final experiments were carried out, traces of impurities in the iron capable of forming volatile oxygen compounds must have been eliminated.

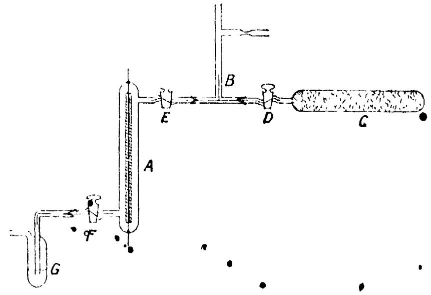

FIG. 75.—Apparatus for analysis of nitrous oxide.

The experimental arrangement adopted for nitrous oxide is indicated in fig. 75. The decomposition vessel A contained the iron spiral, the ends of which were silver-soldered to platinum leads fused into the vessel. Connection with a mercury pump was initially made through B, which was sealed off after A had been completely evacuated. Nitrous oxide was absorbed in C, containing wood charcoal, which had previously been carefully purified by igniting in chlorine, boiling with concentrated hydrochloric acid, washing with water and drying *in vacuo*. The tube C was alternately saturated with nitrous oxide and evacuated several times before being finally charged with the gas. In carrying out an analysis, A was first evacuated and weighed. The apparatus being then fitted up, B was exhausted and sealed off, the spiral heated to bright redness, and by manipulating taps D and E, nitrous oxide was passed, little by little, into A, tap F remaining closed. After the nitrous oxide in A was judged to be completely decomposed, a very slow current of the gas was allowed to pass over the incandescent spiral, the nitrogen escaping by F through the sulphuric acid in G. The current was stopped while a considerable portion of the surface of the spiral still remained unoxidised, D closed and A slowly evacuated by connecting the pump to G;

throughout the evacuation the spiral was maintained at a red heat to ensure the absence of any iron nitride from its surface. Finally, taps E and F were closed, and, on cooling, the increase in weight of the vessel determined. The amount of nitrous oxide used was given by the loss in weight of C.

The decomposition vessel used in the experiments with nitrogen peroxide is shown in fig. 76. It was first evacuated and weighed; pure nitrogen peroxide was distilled into it, and frozen in the tubulure A. The vessel was again exhausted, and the increase in weight, due to the peroxide, was determined. The spiral was then heated to bright redness, and the nitrogen peroxide in the tubulure allowed to evaporate slowly, its vapour being completely decomposed. The residual nitrogen was then pumped out, the spiral being still at a red heat, and finally the vacuous apparatus weighed again, after cooling, in order to determine the weight of the oxygen fixed by the iron.

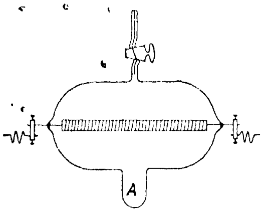

FIG. 76.—Apparatus for analysis of nitrogen peroxide.

For the complete analysis of nitrosyl chloride, the pure, dry vapour was very slowly led through a U-tube containing finely divided silver, heated to 400°–500° C.; special experiments showed that the chlorine was thereby quantitatively retained. The residual nitric oxide was conducted through a second U-tube containing finely divided copper at the same temperature in order to absorb the oxygen; and the nitrogen was finally absorbed by metallic calcium, contained in a straight glass tube heated to redness. Each absorption tube was provided with stopcocks, all connections being made by ground-glass joints according to Morley's method;[1] and a manometer was introduced between the second and third absorption tubes. The entire apparatus was evacuated at the beginning of an experiment, and if the experiment was successful, the apparatus remained vacuous at its termination. Perfect desiccation of the interior of the apparatus was, of course, absolutely necessary; the silver and copper were prepared for use by washing with ether and drying in carbon dioxide and hydrogen respectively, while the calcium was heated to redness *in vacuo*, to eliminate any trace of volatile impurity.

(*b*) *Volumetric Analyses.*—A cylindrical bulb containing an iron spiral and connected by a capillary tube to a mercury manometer formed the apparatus used in the volumetric analysis of nitrous oxide. The manometer was provided with the usual opaque-glass point, to which the mercury was always adjusted whenever a measurement of pressure was required. The bulb was calibrated, and also the "dead space" along the capillary connection as far as the zero-point; and the volumes of gas were corrected for the difference in temperature between that in the bulb and the small amount in the dead space.

The bulb was initially filled with pure, dry nitrous oxide and packed with melting ice; the mercury was then adjusted to the zero-point, the pressure of the gas read (to within 0·02 mm.) and reduced to the value at 0° C. The globe was next dried and the nitrous oxide decomposed by heating the iron spiral to whiteness: to prevent permanent deformation of the bulb, the spiral was repeatedly heated to an exceedingly high temperature, but only for a few seconds at a time, the apparatus being allowed to cool considerably between successive heatings. Each experiment was continued till further heating had no influence on the final volume. Finally, the bulb was allowed to cool, packed around with melting ice, and the pressure of the residual gas observed after adjusting the mercury to zero once more.

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[1] Morley, *Smithsonian Contrib.*, 1895, **29**, No. 980.

The volumetric analysis of ammonia was indirect; the relative volumes of nitrogen and hydrogen which combine to form the gas being deduced from the densities and compressibilities of hydrogen, nitrogen, and the mixture of these gases that results from the decomposition of ammonia. The mixed gases were prepared by generating pure ammonia from ammonium chloride and quicklime, and passing it slowly through a cylindrical tube containing a platinum spiral heated to bright redness. The greater part of the ammonia decomposed; the products passed through a U tube containing glass beads moistened with sulphuric acid to absorb unchanged ammonia, and were dried over phosphoric anhydride. The mixed gases were fed into a volumeter, and the density measured as described later (p. 260).

Density Measurements.—Modern determinations of gas densities[1] have been effected by two methods, (i.) the "globe" method, and (ii.) the "volumeter" method. Each of these was employed by Guye, the former with nitric oxide, and the latter with ammonia, nitrous oxide, and the mixture of nitrogen and hydrogen obtained from ammonia.

In each method the weight of pure, dry gas, which, at an observed temperature (always 0° C. for Guye's measurements) and pressure (approximately atmospheric), occupies a known volume, is determined. The "globe" method has been already outlined (p. 130); the "volumeter" method differs from it in that the measurements of pressure, volume, and temperature are effected in one apparatus, while the gas is weighed in another.[1]

(i.) The "globe" method, first adapted to accurate work by Regnault,[2] is comparatively simple to carry out, permits of several experiments being conducted simultaneously, and furnishes results little, if at all, inferior to those obtained by the volumeter method. It is not necessary to employ very large globes, the results obtained with quite small globes being at least as concordant among themselves as those obtained with 8 to 10 litre globes. Lord Rayleigh's accurate experiments were carried out with a globe the volume of which was about 1·8 litres, while the density of nitric oxide was measured by Gray, using a globe of only 0·267 litre capacity. In their work on the density of nitric oxide Guye and Davila employed three globes of capacities (at 0° C.) 379·80, 385·01, and 817·65 c.c. respectively, calibrated by weighing them empty and then filled with water at 0° C.

A small globe possesses the advantage that the correction necessary on account of its contraction when evacuated is proportionally less than that for a large globe. In fact, the only error that is augmented by employing a small globe is that due to "adsorption" of gas on the surface of the glass.

To obtain accurate results, it is absolutely necessary to have the interior of the globe perfectly dry, and to ensure this, after first repeatedly filling the globe with pure air dried by phosphoric anhydride, it is necessary to fill the globe repeatedly with the pure, dry gas and evacuate. Successive density determinations then give concordant results, provided care is taken to maintain the globe vacuous between the experiments.

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[1] For the "globe" method, *vide* Morley, *loc. cit.*; *Zeitsch. physikal. Chem.*, 1896, **20**, 1; **22**, 2; Rayleigh, *Proc. Roy. Soc.*, 1893, **53**, 134; Leduc, *Ann. Chim. Phys.*, 1898, (vii.), **15**, 5; Gray, *Trans. Chem. Soc.*, 1905, **87**, 1601; Perman and Davies, *Proc. Roy. Soc.*, 1906, **A**, **78**, 28; Baume, *J. Chim. phys.*, 1908, **6**, 1. For the volumeter method, see Morley, *loc. cit.*; Gray and Burt, *Trans. Chem. Soc.*, 1909, **95**, 1633; Perman and Davies, *loc. cit.*

[2] Regnault, *Compt. rend.*, 1845, **20**, 975.

The contraction undergone by each globe when evacuated was directly measured by the method suggested by Travers;[1] for this purpose the globe was supported in the interior of a large desiccator, the stem of the globe passing through one of the holes in a stopper in the desiccator lid. Through the other hole a calibrated vertical capillary tube was passed. The desiccator was filled with water and immersed in a constant temperature bath; and the contraction of the globe was obtained by observing how far the level of the water fell in the capillary tube when the globe was evacuated.[2]

The globes were always filled with nitric oxide at the temperature of melting ice and under a pressure slightly in excess of atmospheric; the tap was opened to allow the pressure to fall to that of the atmosphere, and then closed again. The globe was then dried and weighed against its counterpoise.

The calculation of the results, with all necessary corrections, is explained on p. 130. No correction was applied for "adsorption"; but allowance was made for the deviation of the gas from Boyle's Law.

(ii.) The volumeter method renders it possible to deal with large quantities of gas, since the apparatus for measuring the volume need not be portable. The weight of the gas may be determined in two ways, either by disengaging the gas from an apparatus which only allows pure, dry gas to escape, and determining the loss in weight of the apparatus, or by removing the gas from the volumeter after its volume, temperature, and pressure have been determined, absorbing it by suitable means, and determining the increase in weight of the absorption apparatus and contents. The former method was used for the nitrogen-hydrogen mixture (p. 259); the latter for ammonia and nitrous oxide.

The arrangement adopted by Guye and Pintza is shown in fig. 77. The globes A and B were calibrated by determining the weight of water at 0° C that filled them to the marks *a* and *b*. Their combined volumes amounted to 3502·63 c.c. The "dead space" extending from these marks to the tap L in one direction, and the zero-point *n* of the mercury manometer in the other, was separately determined, as also was the space between the taps H, I, and L.

In conducting an experiment, the absorption tube C, containing cocoanut charcoal, was evacuated, weighed, and attached to the apparatus as shown. The apparatus, which had previously been rinsed out several times with pure, dry gas, was evacuated, and then slowly filled with gas until the pressure was about one atmosphere. The globes were surrounded by melting ice, and when the temperature of the gas had reached 0° C., the taps I and L were closed, the mercury adjusted to the mark *n*, and the initial pressure of the gas accurately observed.

The space H I L was next evacuated, the tap I closed, and then, by suitably manipulating the taps H, L, and R, the gas was absorbed in the charcoal contained in the tube C; this tube was cooled in a bath of ether and solid carbon dioxide. After most of the gas had been absorbed, the taps H and L were closed, and the pressure of the residual gas in the globes determined. The gas contained between H, I, and L, was pumped out and measured, and the absorption tube removed and reweighed.

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[1] Travers, *The Experimental Study of Gases* (Macmillan & Co., 1901), p. 119.

[2] *Cf.* Baume, *J. Chim. phys.*, 1908, 6, 16; this paper contains full details of the experimental methods used at Geneva.

In calculating the results, the difference between the initial and final pressures was taken, and the densities deduced according to the method given on p. 130, the correction for elasticity of the glass is, however, unnecessary. Due allowance was made for the fact that the temperature of the gas in the dead space was not 0° C., and the results were corrected for the known deviations of the gases from Boyle's Law.

Guye and Pintza considered that by still leaving an appreciable amount of gas in the volumeter at the end of an experiment, any "adsorption" effect was eliminated from their results; but this conclusion is erroneous (*cf.* p. 108).

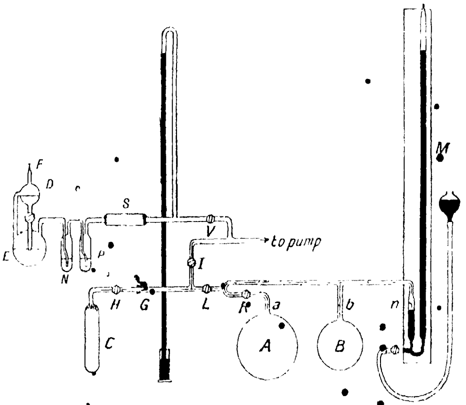

Fig. 77.—Guye's and Pintza's apparatus.

Reference only can be made to the measurements of compressibilities and critical constants (*vide supra*).

Statement of Results. *Analytical Methods*.—(i.) Gravimetric analysis of nitrous oxide. In five experiments,

5·6269 grms nitrous oxide yielded 2·0454 grms. oxygen.

Hence

$$N_2O : O :: 44{\cdot}015 : 16, \text{ and } \mathbf{N = 14{\cdot}008}.$$

The presence of a trace of air or oxides of carbon in the gas would lead to a slightly high value for the atomic weight of nitrogen.

(ii.) Gravimetric analysis of nitrogen peroxide. In seven experiments,

10·3522 grms. nitrogen peroxide yielded 7·1999 grms. oxygen.

Hence

$NO_2 : O_2 :: 46{\cdot}010 : 32$, and N

A trace of oxygen dissolved in the nitrogen peroxide would cause the result to be rather low.

(iii.) Gravimetric analysis of nitrosyl chloride. In five experiments,

0·6067 grm. nitrogen were obtained and 0·6931 grm. oxygen.

Hence

$$N : O :: 14·006 : 16, \text{ and } \mathbf{N = 14·006}.$$

(iv.) Volumetric analysis of nitrous oxide. As the mean of four experiments,

1 litre of nitrous oxide at N.T.P. yielded 1·00717 litres of nitrogen.

But increase in volume of iron spiral, due to oxidation, amounts to 0·30 c.c.; hence corrected volume of nitrogen is 1·00687 litres. Also

1 litre of nitrous oxide at N.T.P. weighs 1·9777 grms. (*vide infra*),
1 „ nitrogen „ „ 1·2507 „ (Rayleigh).

Hence

$$(N_2O - N_2) : N_2 :: 16 : 28·012, \text{ and } \mathbf{N = 14·021}.$$

(v.) Volumetric analysis of ammonia. As the mean of three experiments,

Weight of "normal" litre of mixed hydrogen and nitrogen = 0·3799 grms.

Assuming the data of other observers for the densities and compressibilities of hydrogen and nitrogen, it follows from this result that the molecular volumes of these gases are in the ratio of 1·00057 : 1 at N.T.P., and

$$H_2 : N_2 :: 2·0152 : 28·030, \text{ whence } \mathbf{N = 14·015} \ (H = 1·0076).$$

Guye and Pintza only attach a confirmatory significance to this result, and therefore the details of the calculation are omitted.

Physical Methods: (a) Data.—The values obtained for the weight in grams of a normal litre of gas are as follows:—

NH_3	0·77079	(mean of 5)
N_2O	1·9777	(„ 3)
NO	1·3402	(„ 14)

The following are the values of A_0^1 at 0° C. (see p. 132):—

NH_3.	N_2O.	NO.
+0·01521	+0·00742 (Rayleigh)	+0·00117.

The critical constants are as follows:—

	NH_3.	N_2O.	NO.
Critical temp. (abs.)	405·3°	311·8°	179·5°,
„ press. (atm.)	109·6	77·5	71·2 .

The values for nitrous oxide and nitric oxide are due to Villard[1] and Olszewski[2] respectively.

(b) Calculation of Molecular Weights; Atomic Weight of Nitrogen.—(i.) By Limiting Densities. Assuming the values 1·4290 and +0·00097

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[1] Villard, *Compt. rend.*, 1894, **118**, 1096.

[2] Olszewski, *Phil. Mag.*, 1895, [v.], **39**, 188.

respectively for the normal density and the coefficient A for oxygen, and applying the formula (3) deduced on p. 132, we have :—

	L.	$1 - A_0^1$.	Molecular Weight.	Atomic Weight of Nitrogen.
NH_3 . . .	0·7708	0 98179	17·015	13 992
N_2O . . .	1·9777	0 992..8	44·001	14·001
NO . .	1·3402	0 99883	30·006	14·006
O_2 . . .	1 4290	0·99903	32·000 (standard)	

(ii.) From Critical Constants. Applying the formulæ of p. 131 to the data already given, the following results are obtained :—

	L.	$10^{-5}.a$.	$10^{-5}.b$.	$10^{-5}.a_0$.	$10^{-5}.b_0$.	Molecular Weight.	Atomic Weight of Nitrogen.
NH_3 .	0·7708	859	170	1554	116	17 036	14·013
N_2O .	1·9777	719	185	878	156	44·008	14·004
NO . .	1·3402	257	115	...	.	30·009	14·009

Summary of Results.—The various results obtained by Guye and his collaborators for the atomic weight of nitrogen are given in the following table :—

Analytical.				Physical.			
Gravimetric Analysis.		Volumetric Analysis.		Density Limits.		Critical Constants.	
$N_2O : O$	14 008	$N_2O : N_2$	14·021	NH_3	13·992	NH_3	14·013
$NO_2 : O_2$	14·010	N : 3H	14 015	N_2O	14 001	N_2O	14 004
N : O (in NOCl)	14·006	(indirect)		NO	14·006	NO	14·009

The mean of the three gravimetric values is N = 14·008, much the best series being undoubtedly that relating to the analysis of nitrogen peroxide; in each case the determination was a direct one.

The results of the volumetric analysis confirm the gravimetric value; the value obtained from the analysis of nitrous oxide depends, however, on the densities of nitrous oxide and nitrogen as well as on the volumetric ratio measured, while the uncertainty concerning the value deduced from the analysis of ammonia has been already mentioned.

Turning to the physical results, it is seen that the mean value deduced by the method of critical constants is N = 14·009, in close agreement with the gravimetric value. It should be remembered, however, that this method of calculation is empirical, although it yields good results for a number of other atomic weights (see p. 135).

The results obtained by the method of limiting densities are, in the cases of ammonia and nitrous oxide, distinctly lower than the gravimetric value. These two gases are readily liquefied, and with such gases the molecular weights obtained by this method are usually rather low, probably owing to A_0^1 being overestimated. The method of extrapolating for A_0^1, adopted by Jaquerod and Sheuer for ammonia, is open to criticism; while Rayleigh's value for A_0^1 for nitrous oxide is almost certainly too large, since it is obtained by a linear extrapolation. The value N = 14·006 furnished by nitric oxide is, however, in good agreement with the gravimetric value, as also is the value deduced from the density and compressibility of nitrogen.[1]

The experimental work carried out at Geneva therefore leads to the rounded-off value N = 14·01.[2]

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[1] Berthelot, *Compt. rend.*, 1898, **126**, 954, 1030, 1415, and 1501.

[2] For a full discussion of the atomic weight of nitrogen, see Guye, *Bull. Soc. Chim.*, 1905, **33**, 1; *Chem. News*, 1905, **92**, 261, 275, 285; 1906, **93**, 4, 13, 23, 35; Gray, *Trans. Chem. Soc.*, 1906, **89**, 1174; and for further modern work on the atomic weight of nitrogen, see Gray, *Trans. Chem. Soc.*, 1905, **87**, 1601; Perman and Davies, *Proc. Roy. Soc.*, 1906, **A**, **78**, 28; Richards and Forbes, *J. Amer. Chem. Soc.*, 1907, **29**, 826; Richards, Koethner, and Tiede, *ibid.*, 1909, **31**, 6; Wourtzel, *Compt. rend.*, 1912, **154**, 115. See also Vol. VI. of this series.

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CHAPTER VIII.

CLASSIFICATION OF THE ELEMENTS.

Classification of the Elements.

The educated mind always endeavours to classify and arrange isolated things or ideas. Hence it is not to be wondered at that, when once the Atomic Theory, as enunciated by John Dalton, had been accepted,[1] numerous attempts were made by chemists to discover some method of grouping together those isolated portions of matter known as elements. Of these, the earliest was that of Prout,[2] who, in 1815, suggested his famous hypothesis that the atomic weights of the elements are probably exact multiples of the atomic weight of hydrogen. In Prout's opinion hydrogen corresponded to the πρώτη ὕλη (protyle) of the ancients. This hypothesis was warmly welcomed by Thomas Thomson, who carried out a number of experiments with the direct object of proving the hypothesis to be true.[3] His results, however, were viewed with the greatest suspicion, particularly by Berzelius,[4] who, in 1825, published a revised table of atomic weights, the values for which latter differed very widely from those given by Thomson. In 1829 Edward Turner,[5] a supporter of Prout's hypothesis, confirmed the value ascribed by Berzelius for the atomic weight of barium, proving Thomson's value to be incorrect, and four years later he[6] renounced the hypothesis altogether, as also did Penny in 1837.[7]

The hypothesis was revived, however, by Dumas,[8] who, in conjunction with his pupil Stas, showed that the ratio of the atomic weights of carbon and hydrogen was almost exactly 12 to 1. The atomic weight of chlorine (35·5) was a difficulty, however, and in addition copper, lead, and a few other elements yielded fractions which conscientious chemists could not round off into whole numbers as Thomson had done. To overcome this, Marignac proposed to accept Prout's hypothesis as approximately true only—and in view of the atomic weight of chlorine being, according to his own researches,[1] approximately 35·5—suggested that half the atomic weight of hydrogen might be taken as the unit, a suggestion warmly welcomed by Dumas, who, however, soon found it necessary to halve even this.

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[1] See Chap. I.

[2] Prout, *Ann. Phil.*, 1815, **11**, 321; 1816, **12**, [illegible].

[3] Thomson, *An Attempt to Establish the First Principles of Chemistry by Experiment* (London, 1825).

[4] Berzelius gave most scathing criticisms of Thomson's work. "This investigation," he writes in *Jahresbericht*, 1827, "belongs to that very small class from which science can derive no advantage . . . and the greatest consideration which contemporaries can show to the author is to treat his book as if it had never appeared."

[5] Turner, *Phil. Trans.*, 1829, **119**, 291.

[6] Turner, *ibid.*, 1833, **123**, 523.

[7] Penny, *ibid.*, 1839, **129**, 13.

[8] Dumas and Stas, *Ann. Chim. Phys.*, 1841, **3**, [iii.], 5.

In 1901, however, Strutt[2] raised the question again by showing that the atomic weights, which, according to modern determinations, closely approximate to whole numbers or are actually whole numbers, are far more numerous than the law of chance will allow. In his own words, "the chance of any such coincidence being the explanation is not more than 1 in 1000, so that, to use Laplace's mode of expression, we have stronger reasons for believing in the truth of Prout's Law than in that of many historical events which are universally accepted as unquestionable."[3]

Doebereiner[4] had drawn attention to the fact that certain triads of elements exist, which exhibit both a peculiar regularity in their atomic weights and a close similarity in their chemical and physical properties. For several years the observation was allowed to drop into abeyance, but in 1851 Dumas[5] revived interest in the subject, and several other chemists entered the field, rapidly adding to the list of regularities.

In the following table is given a list of the more important triads which show a constant difference in their atomic weights, the values for the last-named being those published by the International Committee for 1914:—

Element.	Atomic Weight.	Difference.	Mean of Extreme Atomic Weights.
Lithium .	6·94	16·06	
Sodium	23·00	16·10	23·02
Potassium . .	39·10		
Calcium . .	40·09	47·54	
Strontium	87·63	49·74	88·73
Barium	137·37		
Phosphorus .	31·04	43·92	
Arsenic	74·96	45·24	75·62
Antimony	120·2		
Sulphur . .	32·07	47·13	
Selenium	79·2	48·3	79·79
Tellurium . .	127·5		
Chlorine . .	35·46	44·46	
Bromine .	79·92	47·00	81·19
Iodine . . .	126·92		

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[1] Marignac, *Compt. rend.*, 1842, **14**, 570.

[2] Strutt, *Phil. Mag.*, 1901, [vi.], **1**, 311.

[3] See also P. Palladino, *Chem. Zentr.*, 1909, i. 970; Egerton, *Trans. Chem. Soc.*, 1909, **95**, 238; J. Moir, *ibid.*, 1909, **95**, 1752.

[4] Doebereiner, see *Gilbert's Annalen*, 1816, **56**, 332, which contains a report by Wurzer on Doebereiner. See also Doebereiner, *ibid.*, 1817, **57**, 436; and *Pogg. Annalen*, 1829, **15**, 301.

[5] Dumas, *British Assoc. Reports*, 1851; *Compt. rend.*, 1857, **45**, 709; 1858, **46**, 951; 1858, **47**, 1026.

The second group of triads, the atomic weights of which are closely similar to one another, is listed in the following table:—

Iron . .	55·81	Ruthenium .	101·7	Osmium .	190·9
Cobalt . .	58·97	Rhodium . .	102·9	Iridium	193·1
Nickel . .	58·68	Palladium .	106·5	Platinum .	195·2

It was hoped that all the elements might ultimately be grouped into triads, and that in this way a complete system of classification of the elements might be evolved. But there were many elements which could not be brought into line, and when Cooke[1] drew attention to the fact that these triads actually broke up natural groups of elements, a severe blow was struck to their utility. Thus, for example, chlorine, bromine, and iodine are only three out of the four closely related halogens, and a similar objection applies to other triads.

Numerous other regularities and discrepancies were, and have since been, noted in the atomic weights assigned to the elements, but no useful system of classification could be based upon them. Further, many attempts have been made to draw up formulæ whereby the atomic weights of the elements might be calculated, and a check thereby instituted upon the results obtained by experiment. A treatment of these, however, is beyond the scope of this work. The reader wishing to become acquainted with the subject more fully is referred to the original memoirs listed below.[2]

In 1853 Gladstone[3] arranged the elements in the order of increasing atomic weights, but owing to the faulty values at that time accepted as correct, no generalisations of any particular importance were possible. A few years later, however, when the atomic weights had been revised by Cannizzaro, a number of independent investigators discovered that certain remarkable regularities were brought out by arranging the elements in the order of increasing atomic weights. Chancourtois[4] appears to have been the first to observe this, and he arranged the elements in a spiral round a vertical cylinder, whose surface was divided into sixteen vertical sections. The elements situate in any vertical column were seen to possess analogous chemical and physical properties. This arrangement became known as the **Telluric Screw.**

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[1] J. P. Cooke, *Amer. J. Sci.*, 1854, [ii.], **17**, 387.

[2] P. Kremers, *Pogg. Annalen*, 1852, **85**, 56; 1858, **99**, 62. Kotikovsky, *Ueber die Nicht-einfachheit der Metalle, u.s.w.*, 1854, Wien. Lenssen, *Annalen*, 1857, **103**, 121. Odling, *Phil. Mag.*, 1857, [iii.], **13**, 423, 480. Pettenkofer, *Münchener Gelehrten Anzeigen*, 1858, **30**, 261; *Annalen*, 1858, **105**, 188. Mercer, *British Assoc. Reports*, 1858, p. 57. Zaengerle, *Ber.*, 1871, **4**, 570. Waechter, *Ber.*, 1878, **11**, 11. Lersch, *Die Zahlenverhaltnissen des Planetensystems und die Atomgewichte*, 1879, Leipzig. Fedorow, *Bull. Soc. Chim.*, 1882, [ii.], **36**, 559. Bazaroff, *J. Russ. Chem. Soc.*, 1887, **19**, 67. Delauney, *Compt. rend.*, 1888, **106**, 1405; 1907, **145**, 1279. Stransky, *Monatsh.*, 1889, **10**, 19. Adkins, *Chem. News*, 1892, **65**, 123. Hinrichs, *Compt. rend.*, 1893, **116**, 695, 753; *Chem. Zentr.*, 1906, ii. 197; *Compt. rend.*, 1909, **148**, 1760; 1909, **149**, 124, 1074; 1911, **153**, 817. Meusel, *Der Monismus der chemischen Elementen*, Liegnitz, 1893. Lothar Meyer, *Ber.*, 1893, **12**, 1230. J. Thomsen, *Bull. Acad. Denemark*, Dec. 14, 1894. Seubert, *Zeitsch. anorg. Chem.*, 1895, **9**, 334. M. Topler, *Ges. Isis Dresden*, 1896. Abhandlung 4. A. P. Venable, *The Development of the Periodic Law* (Easton, Pa., 1896), gives an interesting account of most of the above, with full references up to 1895. Rydberg, *Zeitsch. anorg. Chem.*, 1897, **14**, 66. L. Dulk, *Ber.*, 1898, **31**, 1865. H. du Bois, *Rapports au Congres Internationale de Physique*, 1900, **2**, 460; H. Biltz, *Ber.*, 1902, **35**, 562. Runge and Precht, *Phil. Mag.*, 1903, [vi.], **5**, 476. E. J. Mills, *Phil. Mag.*, 1903, [vi.], **5**, 543. C. E. Stromeyer, *Mem. Manchester Phil. Soc.*, 1907, **51**, [vi.], 1. N. Delaunay, *Chem. News*, 1908, **97**, 99. D. F. Comstock, *J. Amer. Chem. Soc.*, 1908, **30**, 683. L. Dubreuil, *Compt. rend.*, 1908, **147**, 629; *Bull. Soc. Chim.*, 1909, [iv.], **5**, 660, 708. N. Howard, *Chem. News*, 1910, **101**, 181, 205, 265. J. Moir, *S. African J. Sci.*, 1910, 188. K. Scheringa, *Chem. Weekblad.*, 1910, **7**, 407. Loring, *Chem. News*, 1913, **108**, 247; 1914, **109**, 169; 1914, **110**, 25.

[3] Gladstone, *Phil. Mag.*, 1853, [iv.], **5**, 313.

[4] Chancourtois, *Compt. rend.*, 1862, **54**, 757, 840, 967; 1862, **55**, 600; 1863, **56**, 263, 479; 1866, **63**, 24. See Hartog, *Nature*, 1892, **41**, 186.

About the same time Newlands was working along very similar lines, and in a series of classical papers,[1] introduced his famous generalisation known as **The Law of Octaves.**

At first Newlands' papers were made the subject of ridicule, but before long Lothar Meyer[2] and Mendeléeff,[3] both independently made similar observations. According to Newlands' Law of Octaves, when the elements are arranged in the order of increasing atomic weights, the first and last of any eight consecutive elements possess similar properties; in other words, the properties of the elements are periodic functions of their atomic weights—a generalisation which became known as the **Periodic Law**. At this time, however, not only was the number of known elements relatively small, but the values assigned to their atomic weights were still often faulty. As more elements were discovered, and their atomic weights were determined with greater accuracy, the value of the law became increasingly apparent. The periodic table drawn up by Mendeléeff in 1871 is shown on p. 269, and the modern table, which forms the basis of the classification of the elements adopted in the present series of text-books, is given as the frontispiece. It will be observed that the two tables are substantially the same, save that an extra vertical group has been introduced into the modern table in order to enable the inclusion of the inert gases which, of course, were unknown in 1871. This new group has been appropriately designated as Group 0, for reasons that will be evident later. For the sake of convenience, also, the rare earth elements are included in the modern table in Group III.

A careful examination of these tables reveals the following interesting points:—

In Mendeléeff's table there are two short horizontal series each containing seven elements, no two of which in either separate series resemble one another. But the first, second, etc., members of the first series resemble very closely the corresponding members of the second series; in other words, there is a recurrence of properties with every eighth element.

Passing on to the succeeding horizontal groups, it is observed that it is the alternate elements in the vertical columns that resemble one another most closely. Thus, for example, in Group I., copper and silver are more closely related to one another than are copper and rubidium or than silver and cæsium; and the same is true for rubidium and cæsium. Hence it is customary (see frontispiece) to group together the next two horizontal series as one long series of even and odd members respectively. This arrangement allows of the inclusion of the elements of the eighth group, namely three sets

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[1] Newlands, *Chem. News*, 1864, **10**, 59, 94; 1865, **12**, 83, 94; 1866, **13**, 113, 130. See *On the Discovery of the Periodic Law, and on Relations among the Atomic Weights* (London, 1884).

[2] Lothar Meyer, *Die Modernen Theorien der Chemie*, Breslau, 1864; *Annalen*, 1870, Suppl. **7**, 354; *Ber.*, 1873, **6**, 101.

[3] Mendeléeff, *J. Russ. Chem. Soc.*, 1869, **1**, 60; 1870, **2**, 14; 1871, **4**, 25, 348; *Annalen*, 1872, Suppl. **8**, 130. See also Ostwald's *Klassiker der exakten Wissenschaften*, No. 68, which contains a collection of papers by both chemists.

MENDELÉEFF'S PERIODIC TABLE IN 1871.[1]

Row.	Group I. — R_2O.	Group II. — RO.	Group III. — R_2O_3.	Group IV. RH_4. RO_2.	Group V. RH_3. R_2O_5.	Group VI. RH_2. RO_3.	Group VII. RH. R_2O_7.	Group VIII. — RO_4.
1	H=1							
2	Li=7	Be=9·4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27·3	Si=28	P=31	S=32	Cl=35·5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu'=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	? Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	I=127	
8	Cs=133	Ba=137	? Di=138	? Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	? Er=178	? La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

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[1] See Mendeléeff, *Annalen*, 1872, Suppl., 8, p. 151.

of triads, the elements in each triad possessing approximately the same atomic weights. These are frequently termed transitional elements and connect the even and odd members of the several long series

Turning now more particularly to the modern table (see frontispiece), which, on account of its greater completeness, is worthy of careful study, the following points are observed:—

1. The elements of Group I. and II. exhibit a highly electropositive character, whereas those in Groups VI. and VII. are just as strongly electronegative. Midway between these groups we have carbon and silicon, the two first members of Group IV., which are both electropositive and electronegative upon occasion, and thereby afford excellent justification for retaining their positions.

Disregarding Group VIII. for the moment, we see that the inert gases of Group 0 constitute a very fitting mean between the electronegative elements of Group VII. and the positive elements of Group I.

2. The valencies of the elements in the several groups show a regular increase as we pass from one group to another. Thus, considering the oxygen compounds only, the valencies increase from 0 in Group 0 to 8 in Group VIII. On the other hand, the most stable hydrides are yielded by the elements in Groups IV. to VII., which now exhibit a valency falling from 4 in Group IV. to 1 in Group VII. (see p. 286).

3. All three elements of any one of Doebereiner's triads occur in one or other of the vertical columns. The Periodic Classification thus shows the connection between the various triads themselves, as also the relation between them and the other elements which exhibit no simple uniformity in the numerical values of the atomic weights assigned to them. The advantage of this is stupendous, and in the Periodic System we have the only means as yet discovered of grouping all the elements together as a consistent whole.

4. Numerous blanks occur in the table. Presumably these indicate the existence of hitherto undiscovered elements (see p 275).

5. As a general rule, the metals possess the highest atomic weights.

Not only are the chemical properties of the elements periodic functions of their atomic weights; the same is likewise true for many of their physical characteristics. This is well illustrated by the atomic volumes—that is, the volumes of the gram atoms of the elements in the solid state. In the curves (fig. 78) the atomic volumes are expressed as ordinates, the atomic weights being expressed as the abscissæ, according to the method first proposed by Lothar Meyer. The atomic volumes in the liquid state have been used in the case of elements, such as hydrogen and helium, that are gaseous at ordinary temperatures. A cursory glance suffices to show the symmetrical arrangements of the metals, metalloids, and non-metals, but the system is inferior to the chemical classification already considered, inasmuch as it does not indicate clearly when each curve is complete. Consequently it usually affords but little help either in the search for fresh elements or in the attempt to correct existing atomic weight values.[1]

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[1] Lothar Meyer, *Modern Theories of Chemistry*, translated by Bedson and Williams, (Longmans & Co, 1888); *The Principles of Chemistry*, by Mendeléeff, translated by Kamensky, 1st edition (Longmans & Co., 1892); Hopkins, *J. Amer. Chem. Soc.*, 1911, **33**, 1005. For a number of other atomic weight curves see Wedekind and Lewis, *Atomic Weight Curves* (Stuttgart, 1910).

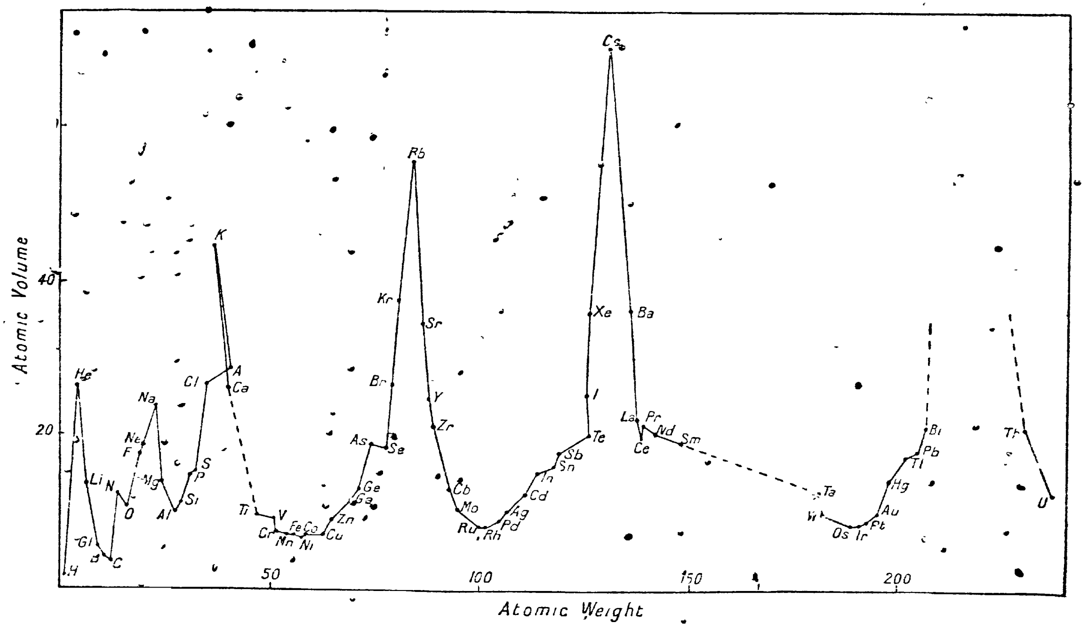

FIG. 78.—Lothar Meyer's atomic volume curve.

Other periodic properties are :—

The crystalline forms of various compounds of the elements.[1]
The melting- and boiling-points of the elements.[2]
Heats of chemical combination.[3]
Valency.[4]
Ionic mobilities.[5]
Changes of volume on fusion.[6]
Ionic colours.[7]
Conductivities.[8]
Hardnesses of the elements.[9]
Distribution of the elements in the earth.[10]
Refractive indices.[11]
Compressibilities.[12]
Densities.[13]
Magnetic susceptibilities.[14]
The spectra of the elements.[15]

With regard to the *spectra*, Kayser and Runge and Rydberg noticed that those elements the spectra of which are known to contain definite line series,[16] may be classified according to the general characteristics of their spectra into exactly the same families as are given by Mendeléeff's table. The spectra of sodium, potassium, rubidium, and cæsium, for instance, all consist of doublet series and correspond with one another almost line for line; and since the "line" P (1) of the lithium spectrum has been shown to be a doublet, it is very probable that all the others are close doublets and that the spectrum is analogous to the spectra of the other alkali metals. Rydberg also noticed that if the common "convergence frequencies" of the two subordinate series in the spectra of the elements, or the limits of the principal series, are plotted against the atomic weights, the points lie on a periodic curve very similar in shape to that obtained by plotting the values of ν/W^2 for D and S doublets, or ν_1/W^2 for D and S triplets, against the atomic weights (W); and further, that not only are the values of ν/W^2 periodic functions of W, but so also are the magnitudes ν themselves.[17]

T. W. Richards has pointed out that the heats of formation of the typical oxides (referred to one-gram equivalent of oxygen), the melting-points and the electrode potentials of the elements, when plotted against the atomic weights, give rise to periodic curves somewhat similar to the atomic volume curve, although the actual "periods" on the curves are different. For instance, the summits on the "heats of formation of the oxides" curve are occupied by Li, Mg, Ca, Sr, La, etc.[1]

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[1] See pp. 70 to 75, where isomorphism is fully dealt with

[2] See Carnelley's numerous papers in *Trans. Chem. Soc.*, *Proc. Roy. Soc.*, and *Phil. Mag.*, from 1876 onwards.

[3] A. P. Laurie, *Phil. Mag.*, 1883, [v.], **15**, 42; Richards, *Trans. Chem. Soc.*, 1911, **99**, 1201.

[4] See p. 286; also Reed, *Trans. St Louis Acad. Sci.*, 1885, **4**, No. 4.

[5] Bredig, *Zeitsch. physikal. Chem.*, 1894, **13**, 289.

[6] M. Topler, *Wied. Annalen*, 1894, **53**, 343.

[7] C. Lea, *Amer. J. Sci.*, 1895, [iii.], **49**, 357.

[8] Sander, *Chem. Zentr.*, 1899, ii. 955, from *Electr. Zeit.*, **6**, 133.

[9] Rydberg, *Zeitsch. physikal. Chem.*, 1900, **33**, 353.

[10] L. de Launay, *Compt. rend.*, 1904, **138**, 712; V. Poschl, *Zeitsch. physikal. Chem.*, 1908, **64**, 707.

[11] F. L. Bishop, *Amer. Chem. J.*, 1906, **35**, 84.

[12] T. W. Richards, W. N. Stull, F. N. Brink, and F. Bonnet, *Carnegie Inst. Publication*, 1907, No. 76; *Zeitsch. Elektrochem.*, 1907, **13**, 519; *Zeitsch. physikal. Chem.*, 1907, **61**, 77, 100; *J. Amer. Chem. Soc.*, 1909, **31**, 154; E. Gruneisen, *Ann. Physik*, 1908, [iv.], **26**, 393.

[13] Poschl, *Zeitsch. anorg. Chem.*, 1908, **59**, 102.

[14] M. Owen, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 637.

[15] See Kayser and Runge, *Wied. Annalen*, 1890, **41**, 302; 1891, **43**, 385. Rydberg, *K. Svenska Vet-Akad. Handl.*, 1890, **23**, No. 11; *Wied. Annalen*, 1893, **50**, 629; *Astrophysical J.*, 1897, **6**, 233; Baly, *Spectroscopy* (Longmans & Co., 1905), Chap. xv.

[16] See pp. 235 and 239.

[17] Rydberg, *loc. cit.*, and *Paris International Reports*, 1900, **2**, 200.

Imperfections of the Periodic Classification.—It is not surprising that a system of classification which aims at embracing not only all the known but also the unknown elements existing either in the free state or in various stages of combination in the universe, should have its weak points. These may arise from two causes, namely:—

1. An imperfect knowledge of the law itself, which either leads us to seek too wide an application for it, or to limit its sphere of activity by seeking to confine it within certain narrow and arbitrary boundaries.

2. Insufficient or inaccurate knowledge of the elements it is sought to include within the scope of the law.

As a matter of fact cases have arisen from both of these causes. Thus, when the inert gases were discovered, there was no place for them in the table until the system had been expanded by the inclusion of a separate vertical column, now known as Group 0.[2] This extension not only makes the system more complete by reducing the abruptness of the change as we pass from the highly electronegative elements of Group VII. to the equally highly positive members of Group I., but it also widens the scope by yielding a series of blank spaces which may in the future be filled in with the names of elements not yet discovered.

As an example of discrepancies arising from the second cause, namely, insufficient or inaccurate knowledge of the elements themselves, the case of osmium, iridium, and platinum may be mentioned.

In 1870 these elements were believed to have the following atomic weights:—

Osmium	198·6
Iridium	196·7
Platinum	196·7

According to this, their positions in Group VIII. should be reversed, platinum coming under the same vertical column as iron and ruthenium, the metal osmium being relegated to the third vertical column, under nickel and palladium. But such an arrangement is opposed to the general properties of these elements, platinum resembling nickel and palladium more closely than it does iron and ruthenium, the reverse being true for osmium. Subsequent research, however, has shown that the atomic weights assigned to the above three elements in 1870 were inaccurate, the values recognised by the International Atomic Weight Committee for 1917 being as follows:—

Osmium	190·9
Iridium	193·1
Platinum	195·2

The discrepancy, therefore, no longer exists.

There still remain, however, a few remarkable exceptions to the law. These are as follows:—

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[1] T. W. Richards, The Faraday Lecture, *Trans. Chem. Soc.*, 1911, 99, 1201.

[2] Ramsay, *Ber.*, 1898, 31, 3111. See Part II. of this Volume.

1. *Argon and Potassium.*—With an atomic weight of 39·88, argon should lie between potassium and calcium in the periodic table. But there is no room for it, and to interchange the positions of argon and potassium by placing the latter element in Group 0, and the former in Group I., would obviously destroy the symmetry of the whole (see this volume, Part II.).

2. *Tellurium and Iodine.* — From chemical considerations tellurium properly belongs to Group VI. and iodine to Group VII.; but the atomic weight of the former element is found to be higher than that of iodine, which implies that the positions of these elements in the table should be reversed (see Vol. VII.).

3. *Nickel and Cobalt.*—The atomic weight of nickel, as determined in a variety of ways, is slightly less than that of cobalt, a result which places it between iron and cobalt in the eighth group. Nickel, however, resembles palladium and platinum more closely than it does rhodium and iridium, the reverse being true for cobalt. Furthermore, by placing cobalt between iron and nickel, a more gradual variation in the properties of the three elements becomes observable. Thus, for example, whilst iron forms two series of well-defined salts, namely the ferric salts, cobalt forms cobaltic salts only with comparative difficulty, and nickel only yields nickelous salts. Evidently, therefore, the true position of cobalt should lie between iron and nickel (see Vol. IX.).

In addition to the above anomalies there are several indications that the periodic system is not perfect as it stands at present. Of these the following are the most important:—

1. *The Position of Hydrogen.*—It is generally agreed that the valency of hydrogen is unity, and this opens up two possible positions for the element in the table, namely at the head of either the first or the seventh group. In accordance with its low boiling-point, and the diatomic nature of its gaseous molecule, many chemists prefer to include hydrogen in the seventh group along with the halogens; and this is apparently justified by the fact that solid hydrogen bears no resemblance whatever in its physical properties to the alkali metals,—on the contrary, it is typically non-metallic. Furthermore, Moissan[1] showed that in the metallic hydrides hydrogen [illegible] like a non-metal, inasmuch as the hydrides do not conduct [illegible] and hence cannot be regarded as comparable with [illegible] chemical behaviour of hydrogen is considered, facts [illegible] of its metallic nature. The most stable compounds of [illegible] metals generally, are those formed by union with [illegible] its. Thus, for example, although the halogens exhibit [illegible] to combine amongst themselves, save in the case of the tw[illegible]nts, fluorine and iodine, yet they yield very stable compounds [illegible] and the metals. The same truth applies with more or [illegible] to the other non-metallic elements known. Consequently it [illegible] most natural to regard hydrogen as analogous to a metal, a[illegible] is a more fitting forerunner of the alkali metals than of the halogens. [illegible] present series of text-books, therefore, hydrogen will receive detailed treatment in Vol. II.

2. *Group VIII.* is anomalous in that it is the only one containing more than one element along each horizontal line. Although these several triads serve, as already mentioned, to connect the odd and even members of the three long series, their function in this capacity is doubtful, and somewhat destroys the symmetry of the whole (see Vol. IX.).

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[1] Moissan, *Compt. rend.*, 1903, 136, 591.

3. *The Rare Earth Metals* (see Vol. IV.).—These comprise some thirteen elements—namely cerium, dysprosium, erbium, europium, gadolinium, holmium, lutecium, neodymium, praseodymium, samarium, terbium, thulium, and ytterbium,—whose atomic weights lie between those of lanthanum (139) and tantalum (181). Now although a considerable number of blank spaces occur in the table between the positions usually assigned to lanthanum and tantalum, yet if we attempt to fit the rare earths into these in the usual manner, the result is most unsatisfactory, and destroys the symmetry and harmony of the whole. This difficulty may be partly overcome by assuming that the rare earths are all trivalent, and grouping them together in the third vertical column. Although this arrangement is not ideal, there is much in its favour, and, for the sake of convenience, it is the one adopted in the present series of text-books.

Advantages of the Periodic Classification.—1. *It affords the only known method of satisfactorily classifying the elements.*

2. *By means of the Periodic System the atomic weights of the elements may be determined when their equivalent or combining weights are known.* This is a most important feature of the system and was used to good purpose in the case of glucinum. The combining weight of this element was found to be 4·55, and, owing to its apparent resemblance to aluminium, Berzelius[1] regarded it as trivalent, and its atomic weight was in consequence taken as 3 × 4·55, namely 13·65. According to the periodic classification, therefore, the element should lie between carbon (C = 12·00) and nitrogen (N = 14·01); but there is no room for it. If, however, we assume the element to be divalent, its atomic weight is reduced to 2 × 4·55 = 9·1, which brings the element between lithium and boron. Here we not only have a vacancy, but other elements grouped together in the same column have properties analogous to those of glucinum. This, therefore, is its proper place (Vol. III.).

3. *The Correction of Inaccurate Values for the Atomic Weights.*—As examples of this we have already mentioned osmium, iridium, and platinum.

4. *The Prediction of the Discovery of New Elements, and an Indication of their General Chemical Characteristics.*—The numerous blanks in the periodic table are generally assumed to indicate the existence of hitherto undiscovered elements. Previous to 1875 there were three gaps in the table pointing to the existence of three elements at that time unknown, the atomic weights of which were less than 75. Two of these occurred in Group III. immediately below aluminium, and one in Group IV. below titanium. To these hypothetical elements Mendeléeff gave the names of eka-boron, eka-luminium, and eka-silicon, respectively, and by studying the known elements in the immediate neighbourhood of the gaps, he was able to give in considerable detail the properties which these elements would be found to possess. His predictions were verified in a remarkable manner less than twenty years after publication in the discovery by Lecoq de Boisbaudran in 1875 of gallium, possessing all the properties of eka-luminium; of scandium (eka-boron) by Nilson in 1879; and of germanium (eka-silicon) by Winkler in 1887. (See Vols. IV. and V.)

Modifications of the Periodic System. The obvious weaknesses of the Periodic System, as detailed in a preceding section of this chapter, have led to the advancement of a surprising number of modifications and improvements (!). We have not space to deal with these here, but the reader desirous of pursuing the subject further is referred to the appended list of references, which is fairly complete.[1]

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[1] Berzelius, Schweigger's *Journ. Chem. Pharm.*, 1816, 17, 296.

THE STRUCTURE OF THE ATOM AND ITS BEARING ON THE PERIODIC CLASSIFICATION.

According to the modern view of atomic structure,[2] an atom consists of a central core or *nucleus* of very small dimensions, in which practically all the mass of the atom is concentrated, and a number of *electrons* arranged in layers around the nucleus and extending from it to distances comparable with the ordinarily accepted radius of the atom. There is but one kind of electron, common to all kinds of matter; it carries a charge of negative electricity, termed the unit charge, and its mass is about 1/1700 of that of an atom of hydrogen. The nucleus of a neutral atom carries a positive charge equal to the sum of the charges on the surrounding electrons; but although the nucleus carries a net positive charge, it may contain negative electrons within its structure. When a radioactive atom undergoes disintegration the α and β particles it emits[1] are considered to come from the nucleus.[2] The mass of an atom is regarded as being approximately proportional to the charge on the nucleus.

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[1] Baumhauer's Spiral Arrangement—Baumhauer, *Die Beziehungen zwischen dem Atomgewichte und der Natur der chemischen Elemente*, p. 23 (Brunswick, 1870). Concentric Ring Arrangement—Wiik, *Forsok till en pä Atomgewigten Grundad Grupperung af de kemiska Elementerna* (Helsingfors, 1875). Von Huth's Spiral—E. von Huth, *Das periodische Gesetz der Atomgewichte und das naturliche System der Elemente* (Frankfurt, 1884). Carnelley, *British Association Reports*, 1885; *Phil. Mag.*, 1890, [v.], **29**, 97. W. Spring, *Tableau representant la Loi Periodique des Éléments Chimiques* (Liège, 1881); see *Periodic Law*, by Venable (Chemical Publishing Co., Easton, Pa.), 1896, where the scheme is reproduced. J. Emerson Reynolds, *Chemical News*, 1886, **54**, 1; *Trans. Chem. Soc.*, 1902, **81**, 612. T. Bayley, *Phil. Mag.*, 1882, [v.], **13**, 26. Crookes, *Chem. News*, 1886, **54**, 117; *Trans. Chem. Soc.*, 1888, **53**, 487; see also *ibid.*, 1889, **55**, 257. Livermore, *Proc. Amer. Acad.*, 1888, **24**, 164. J. Stoney, *Chem. News*, 1888, **57**, 163; *Phil. Mag.*, 1902, [vi.], **4**, 411. Haughton, *Chem. News*, 1888, **58**, 93, 102. Tchitcherine, *Bull. Soc. Imp. de Nat. de Moscow*, 1890, 1. Sutherland, *Phil. Mag.*, 1890, [v.], **30**, 318. J. Walker, *Chem. News*, 1891, **63**, 251; *Introduction to Physical Chemistry* (Macmillan & Co.), 1899. W. Preyer, *Berlin Phys. Ges.*, 1891, **10**, 85; *Berlin Pharm. Ges.*, 1892, 144; *Das Genetische System der Chemischen Elemente*, Berlin, 1893, p. 104. Bassett, *Chem. News*, 1892, **65**, 3, 19. Weeley, *Trans. Chem. Soc.*, 1893, **63**, 852; *Proc. Chem. Soc.*, 1896, **12**, 185. Rang, *Chem. News*, 1893, **67**, 178. J. Traube, *Ber.*, 1894, **27**, 3179. A. P. Venable, *J. Amer. Chem. Soc.*, 1895, **17**, 75; see also Venable's *Development of the Periodic Law*, 1896 (Chemical Publishing Co., Easton, Pa.), where full references up to 1895 are given. Lecoq de Boisbaudran, *Chem. News*, 1895 **71**, 271; *Compt. rend.*, 1897, **124**, 127. J. Thomsen, *Zeitsch. anorg. Chem.*, 1895, **9**, 190, 283. K. Seubert, *Zeitsch. anorg. Chem.*, 1895, **9**, 334. Delauney, *Compt. rend.*, 1896, **123**, 600. Flavitzky, *Zeitsch. anorg. Chem.*, 1896, **12**, 182. E. Loew, *Zeitsch. physikal. Chem.*, 1897, **23**, 1. Wilde, *Compt. rend.*, 1897, **125**, 707. Richards, *Amer. Chem. J.*, 1898, **20**, 543. Ramsay, *Ber.*, 1898, **13**, 311; *Modern Chemistry*, 1900, p. 50; *The Gases of the Atmosphere*, 1902 (Macmillan & Co.). G. Rudorf, *The Periodic Classification and the Problem of Chemical Evolution*, 1900 (Whittaker & Co.), contains full references to literature. K. Smireisen, *Zeitsch. physikal. Chem.*, 1900, **33**, 63. Armstrong, *Proc. Roy. Soc.*, 1902, **70**, 86. H. Biltz, *Ber.*, 1902, **35**, 562. Staigmüller, *Zeitsch. physikal. Chem.*, 1902, **39**, 243. Brauner, *Zeitsch anorg. Chem.*, 1902, **32**, 18. A. Werner, *Ber.*, 1905, **38**, 914; *Neuere Anschauungen auf dem Gebicte der anorganischen Chemie* (Vieweg, Brunswick), 1905. R. Abegg, *Ber.*, 1905, **38**, 1386. C. Zenghelis, *Chem. Zeit.*, 1906, **25**, 294, 316. G. Woodiwiss, *Chem. News*, 1906, **93**, 214; 1908, **97**, 122. A. Minet, *Compt. rend.*, 1907, **144**, 428. Loring, *Chem. News*, 1909, **99**, 148, 167, 241; 1909, **100**, 37, 120, 281; *Physikal. Zeitsch.*, 1911, **12**, 107. A. T. Cameron, *Nature*, 1909, **82**, 67. J. F. Tocher, *Pharm. J.*, 1910, [iv.], **31**, 159. C. Schmidt, *Zeitsch. physikal. Chem.*, 1911, **75**, 651. B. K. Emerson, *Amer. Chem. J.*, 1911, **45**, 160. E. Bauer, *Zeitsch. physikal. Chem.*, 1911, **76**, 569. Toribio Cáceres, *Anal. Fis. Quim.*, 1911, **9**, 82, 121. E. Q. Adams, *J. Amer. Chem. Soc.*, 1911, **33**, 684. K. Scheringa, *Chem. Weekblad*, 1911, **8**, 389, 868. E. von Stackelberg, *Zeitsch. physikal. Chem.*, 1911, **77**, 75. A. van den Broek, *Physikal. Zeitsch.*, 1911, **12**, 490. Rayleigh, *Proc. Roy. Soc.*, 1911, A, **85**, 471. F. Sanford, *Phys. Review*, 1911, **32**, 512; *J. Amer. Chem. Soc.*, 1911, **33**, 1349. Loring, *Chem. News*, 1915, **111**, 13, 157, 181; Buchner, *Chem. Weekblad.*, 1915, **12**, 336. Rydberg, *J. Chim. phys.*, 1914, **12**, 585. Harkins and Hall, *J. Amer. Chem. Soc.*, 1916, **38**, 169.

[2] Rutherford, *Phil. Mag.*, 1911, [vi.], **21**, 669; 1914, [vi.], **27**, 488; Sir J. J. Thomson, *ibid.*, 1904, [vi.], **7**, 237; 1906, [vi.], **11**, 769; *The Atomic Theory* (Clarendon Press, 1914).

Although an atom such as has been described is electrically neutral, it will nevertheless produce a field of electric force in its neighbourhood, which force will be exerted on other atoms associated with it in a chemical molecule. Its range of effective action will also extend to neighbouring molecules, and thus forces between molecules will arise and account for such physical phenomena as the intrinsic pressure and surface tension of liquids, the cohesion of solids and liquids, etc.

The electrons in the outer layer are considered to be held in position less firmly than the others. They are mobile and arrange themselves easily under the influence of forces exerted on them by other atoms; and some of them may be detached from the atom and transferred to another. The chemical properties of an atom and such physical properties as those mentioned in the preceding paragraph will therefore depend mainly on the outer layer of electrons, and, owing to the manner in which the positions of these electrons vary, these properties will vary with the kinds of other atoms with which it is associated. The electrons in the inner layer, however, are much more firmly held and are little affected by the proximity of other atoms properties of the atom associated with these electrons will therefore b independent of the nature of other atoms that may associate with the atom in question.

Reverting now to the discrepancies in the Periodic Law associated with the positions of argon and potassium, nickel and cobalt, and iodine and tellurium, it may be said that in the cases of the last two pairs there is little or no prospect that subsequent work will change the order of the atomic weights. The conclusion therefore appears inevitable that the position of an element in the Periodic Table is not dependent upon its atomic weight, but rather upon some other property of the atom to which the atomic weight is approximately proportional. Pursuing this line of thought, it may be further supposed possible, and even probable, that when this property of the atom is identified it will be found that its value steadily changes by equal increments from one element to the next when they are arranged in the accepted order of appearance in the Periodic Table. The successive atomic weight differences, on the other hand, being known to be not even approximately equal, it would then occasion no surprise if the order of the elements in the table did occasionally clash with the sequence of atomic weights.

There is considerable evidence that the view outlined in the preceding paragraph (or some very similar view) is correct and that the "unknown" property of the atom is to be identified with the charge on the positive nucleus of the atom or, what is proportional to it, the number of electrons surrounding the positive nucleus of the neutral atom. This is essentially what is known as Van den Broek's Hypothesis and is usually expressed with reference to the so-called "atomic numbers" of the elements. The hypothesis may be stated in the following manner: If the elements are arranged in increasing order of number of electrons surrounding the positive nucleus of the neutral atom and numbered in order 1, 2, 3, etc., then these numbers, which are called the *atomic numbers* of the elements, are identical with the numbers of free electrons in the corresponding neutral atoms and also with the numbers of the places occupied by the elements in the Periodic Table when hydrogen, helium, lithium, etc., are assigned the places 1, 2, 3, etc.[1]

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[1] The α particle is a helium atom associated with two negative charges, and the β particle is a negative electron.

[2] See, *e.g.*, Rutherford, *loc. cit.*; Bohr, *Phil. Mag.*, 1913, [vi.], **26**, 1, 476, 857; Fleck, *Trans. Chem. Soc.*, 1914, **105**, 247.

Owing to the fact that it is not known with certainty how many rare earth elements and inert gases actually exist, it is not possible to state the exact atomic numbers of the elements of high atomic weight. So far, however, as the elements from thallium to uranium are concerned, it is practically certain that the nuclear charges of their atoms increase by one unit at a time on passing from one element to the next in the Periodic Table—a result in accordance with Van den Broek's Hypothesis. This follows at once from a consideration of the known radioactive transformations, provided that the highly probable assumption is made that the α and β rays are expelled from the nuclei of the atoms.[2]

The work of Moseley on the X-ray spectra of the elements brings many more elements within the scope of Van den Broek's Hypothesis. X-rays are emitted by an element when the element or one of its compounds is bombarded with cathode rays, and, by taking advantage of Bragg's discovery (p. 50) that the X-rays are reflected at crystal faces it is possible to examine their spectra. The X-ray spectra of the elements contain only a few lines, of extremely short wave-length, and Moseley found that when the square roots of the wave numbers (p. 234) of the lines in all the spectra are plotted in one diagram against the atomic numbers of the elements the points lie on a series of smooth curves which approximate closely to straight lines. There are accordingly corresponding lines in the X-ray spectra of different elements, and the wave numbers of the lines in any one group of corresponding lines may be reproduced with considerable accuracy by a formula of the simple type

$$n = A(N - b)^2,$$

where n is the wave number and A and b are constants, by assigning to N the successive values of the atomic numbers. Since the X-ray spectrum of an element undoubtedly depends upon the charge associated with the positive nucleus of its atom, Moseley's results afford valuable evidence in favour of Van den Broek's Hypothesis; and one particularly interesting result of this work is that it establishes the atomic numbers of potassium, argon, nickel, and cobalt, which are found to be in accordance with the positions always assigned to them in the Periodic Table and not in accordance with the atomic weights sequence.[3]

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[1] Van den Broek, *Nature*, 1911, **87**, 78; 1913, **92**, 373, 476; *Physikal. Zeitsch.*, 1912, **14**, 32; *Phil. Mag.*, 1914, [vi.] **27**, 455.

[2] Soddy, *Jahrb. Radioaktiv. Electronik.*, 1913, **10**, 188; *Chem. News*, 1913, **107**, 97.

[3] Moseley, *Phil. Mag.*, 1913, [vi.], **26**, 1024; 1914, [vi.], **27**, 703.

It may be also mentioned that the nuclear charge of an atom of an element may be estimated by determining the power of the element to scatter α or X-rays, and that the results, which indicate that the nuclear charge is equal to about one-half the atomic weight of the element, are in fair accordance with Van den Broek's Hypothesis.[1]

RADIO-ELEMENTS AND THE PERIODIC CLASSIFICATION

Although the discovery of the radio-elements has made it difficult to define precisely what is to be understood by an element, it nevertheless still remains true that those species of matter known as elements undoubtedly form a distinct group of substances and that the radio-elements thorium, radium, and uranium, which find places in the Periodic Table, belong to that group. There is, therefore, no logical reason for denying the title of element to each of the other radio-elements and no apparent reason why all the radio-active elements should not find places in the Periodic Table. Since, however, on the disintegration theory all the radio-elements derived from thorium or uranium must have smaller atomic weights than thorium or uranium respectively, an obvious difficulty arises since there are practically no available vacant places in the table.

The names of the radio elements, the symbols in common use for them, and their atomic weights are given in the following table:—

THE RADIO-ELEMENTS.

Element.	Symbol.	Atomic Weight.	Element.	Symbol	Atomic Weight.
Thorium	Th	232·4	Radium A	RaA	218·0
Mesothorium I	MsThI	228·4	Radium B	RaB	214·0
Mesothorium II	MsThII	228·4	Radium C	RaC	214·0
Radiothorium	RaTh	228·4	Radium C_1	RaC_1	214·0
Thorium X	ThX	224·4	Radium C_2	RaC_2	210·0
Thorium Emanation	ThEm	220·4	Radium D	RaD	210·0
Thorium A	ThA	216·4	Radium E	RaE	210·0
Thorium B	ThB	212·4	Radium F	RaF	210·0
Thorium C	ThC	212·4	Actinium	Ac	(226)
Thorium C_1	ThC_1	212·4	Radioactinium	RaAc	(226)
Thorium D	ThD	208·4	Actinium X	AcX	(222)
Uranium	U	238·0	Actinium Emanation	AcEm	(218)
Uranium X_1	UX_1	234·0	Actinium A	AcA	(214)
Uranium X_2	UX_2	234·0	Actinium B	AcB	(210)
Uranium II	UII	234·0	Actinium C	AcC	(210)
Ionium	Io	230·0	Actinium C_1	AcC_1	(210)
Radium	Ra	226·4	Actinium D	AcD	(206)
Niton	Nt	222·4			

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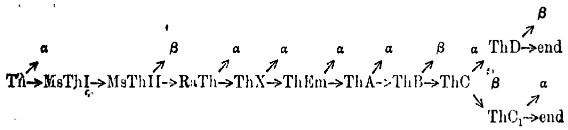
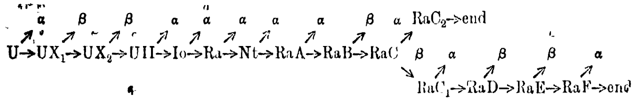
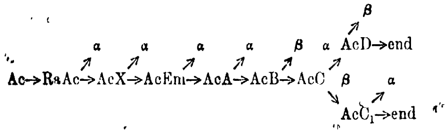
[1] Geiger and Marsden, *Proc. Roy. Soc.*, 1909, **A**, **82**, 495; Geiger, *ibid.*, 1910, **A**, **83**, 492; Barkla, *Phil. Mag.*, 1911, [vi.], **21**, 648; for a further account of Van den Broek's Hypothesis see, in addition to the previous references to this section, J. W. Nicholson, *Phil. Mag.*, 1914, [vi.], **27**, 541, where the hypothesis is criticised in some detail. For a summary, see *Chem. Soc. Ann. Report* for 1913, **10**, 270. Sir J. J. Thomson has suggested that it may perhaps be necessary to divide the elements into two groups and apply a modified form of Van den Broek's hypothesis to each group (Sir J. J. Thomson. *The Atomic Theory* (Clarendon Press, 1914)).

The atomic weights here given are based upon the following assumptions:—(i.) that mass is conserved in radioactive changes, (ii.) that the atomic weights of radium and thorium are 226·0 and 232·4 respectively,[1] (iii.) that the expulsion of an α particle from an atom leaves behind a new atom of atomic weight 4 units less, (iv.) that the expulsion of a β particle leaves behind an atom of the same atomic weight as before, and (v.) that the atomic weights of actinium and radium are equal—an assumption which is open to some doubt.[2]

The manner in which the radio-elements arise from the parent elements thorium, uranium, and actinium[3] is indicated in the following schemes, one or two of the details of which are still (1914) rather dubious:—







With regard to the end-products, it has long been regarded as certain that the uranium end-product is lead, and there is direct evidence in favour of this view, although the evidence is not conclusive.[4]

It has been mentioned in the preceding section that a study of the radioactive transformations shows that, so far as the elements from thallium to uranium are concerned, the charge on the positive nucleus of the neutral atom increases by one unit at a time in passing from one place in the Periodic Table to the next—a conclusion in harmony with Van den Broek's Hypothesis. Suppose, now, that this regularity holds for all the radio-elements. It is then easy to assign places in the table to all the members of the uranium and thorium series, for the position of a radio-element will be two places before or one place after that of its parent according to whether its atom is produced from that of its parent by loss of an α or a β particle; when this is done the positions of niton and radium, defined by the preceding rule, and the known position of uranium, agree with those which would be chosen from purely chemical reasons. It frequently happens, however, that several elements fall into the same place in the table. The remarkable observation has been made that all the elements occurring together in the same place in the Periodic Table appear to be identical in their chemical and many of their physical properties and cannot be separated by chemical means. They are said to be *isotopes* or to be *isotopic* with one another. Isotopy was first recognised by Soddy for radium and mesothorium I.[1]

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[1] See Vols. III. and V.

[2] Fajans, *Le Radium*, 1913, 10, 171.

[3] It is very improbable that actinium is a "parent" element, but its progenitor is unknown.

[4] Gray, *Nature*, 1913, 91, 659.

The positions of the members of the actinium series may now be determined by finding their isotopes. When these have thus been found, the last two rows of the Periodic Table appear as shown in the accompanying table.

Row.	Group 0.		Group I.		Group II.		Group III.		Group IV.		Group V.		Group VI.		Group VII.	
	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.
11				Au		Hg		Tl AcD ThD RaC_3		UEnd AcEnd Pb ThEnd RaD ThB RaB		Bi RaE AcC ThC RaC		RaF AcC_1 ThC_1 RaC_1 AcA ThA RaA		
12	AcEm ThEm Nt				AcX ThX Ra MsThI		Ac MsThII		RaAc RaTh Io Th UX_1		UX_2		UII U			

If the view here outlined be correct, it affords convincing evidence that the property which defines the position of an element in the Periodic Table is not its atomic weight, but an electrical property associated with its atom. A group of isotopes is a group of elements the atoms of which carry the same charge on their positive nuclei, *i.e.* they have the same atomic number; and this result is quite intelligible since the nuclear charges are only net charges indicating in each case an excess of positive electricity over the negative charges of the electrons contained in the nucleus, and the different nuclei may contain different numbers of negative electrons. The chemical properties of the radio-elements are in harmony with their positions in the Periodic Table indicated in the diagram. The element UX_2, for example, is quite analogous to tantalum, its predecessor in Group V (column A) of the table. Since this element occupies a place in the table by itself, it has been given a distinctive name, *brevium*.[2]

The final, stable, non-radioactive elements that result from the disintegration of thorium, uranium, and actinium, are seen to be isotopic with lead. In the cases of thorium and uranium, the atomic weights of these end-products are calculated to be 208·4 and 206·0 respectively, and in order to make these two atomic weights equal it is necessary to change the atomic weights of thorium and radium by amounts much greater than their uncertainties appear to be. The atomic weight of lead is 207·20, and the question therefore arises whether ordinary lead may not be a mixture of isotopes. In such a case the atomic weight of lead would vary with its origin. This was first shown to be the case by Soddy and Hyman,[1] and their conclusion has been confirmed by several other investigators.[2] The sources and atomic weights of the various preparations of radioactive lead that have been examined are detailed in the following table:—

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[1] Soddy, *Trans. Chem. Soc.*, 1911, 99, 72.

[2] Fajans and Göhring, *Physikal. Zeitsch.*, 1913, 14, 877.

Lead extracted from—	Soddy and Hyman	Richards and Lembert.	Honigschmid and Horovitz.	Curie.
Thorite (Ceylon)	208·4	..	..	..
Thorianite (Ceylon)	.	206·82	..	..
Pitchblende (Joachimsthal)	..	206·57	206·405	206·64
„ (Cornwall)	..	206·86	.	..
Uraninite (N. Carolina)	..	206·40		..
„ (E. Africa)	..		206·046	..
Bröggerite (Norway)	..	..	206·063	..
Carnotite (Colorado)	..	206·59	..	206·36
Monazite	..	..	..	207·08
Yttro-tantalite	..	.	.	206·54
(Non-radioactive source)	207·1	207·15	207·180	207·01

Moreover, the lead extracted from carnotite possesses an ultra-violet spectrum identical with that of ordinary lead (Richards and Lembert). In no other case has the atomic weight of an element been found to vary with its geographical source, although the possibility of such variation has been recognised and experimental evidence on the subject sought by various investigators.[3] Further experiments in this direction promise to be of exceptional interest.[4]

VALENCY.[5]

Introductory.—A number of elements form hydrides of known molecular formulæ. The formulæ of those hydrides in which there is only one atom of the element other than hydrogen in the molecule are given in the following table:—

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[1] Soddy and Hyman, *Trans. Chem. Soc.*, 1914, 105, 1402.

[2] T. W. Richards and Lembert, *J. Amer. Chem. Soc.*, 1914, 36, 1329. Honigschmid and Mdlle. Horovitz, *Compt. rend.*, 1914, 158, 1796. *Monatsh.*, 1915, 36, 355. M. Curie, *Compt. rend.*, 1914, 158, 1676.

[3] See, *e.g.* Baker and Bennett (*Trans. Chem. Soc.*, 1907, 91, 1849) and Lenher (*J. Amer. Chem. Soc.*, 1909, 31, 20) on tellurium; Richards (*Proc. Amer. Acad.*, 1887, 23, 177) on copper; Richards (*J. Amer. Chem. Soc.*, 1902, 24, 374) on calcium; Richards and Wells (*ibid.*, 1905, 27, 459) on silver and sodium; Baxter and Thorvaldson (*ibid.*, 1911, 33, 337) on iron.

[4] The arrangement of the radio-elements in the Periodic Table as here described is that given by F. Soddy, to whose interesting little book, *The Chemistry of the Radio-Elements*, Part 2 (Longmans & Co., 1914), the reader is referred for full details and references to the literature. The arrangement is due largely to the work of Soddy, Fajans, Fleck and Russell, and it should be mentioned that it was not arrived at directly from Van den Broek's Hypothesis, as the text may seem to imply, and does not stand or fall with that hypothesis.

[5] For further information on the subject of Valency than can be given here, the reader is referred to Friend, *Theory of Valency* (Longmans & Co., 1909); Hinrichsen, *Ueber den gegenwärtigen Stand der Valenzlehre* (Ahrens's Sammlung, No. 7, 1902); Morley and Muir's *Dictionary of Chemistry*, articles on Equivalency and Isomerism; and the chapters on Valency in the *Study of Chemical Composition* (Cambridge University Press, 1904) by Miss Freund; Muir, *History of Chemical Theories and Laws* (Wiley & Sons, 1907), etc.

HF	H_2O	H_3B	H_4C
HCl	H_2S	H_3N	H_4Si
HBr	H_2Se	H_3P	H_4Ge
HI	H_2Te	H_3As	
		H_3Sb	

An element M which forms a hydride of molecular formula MH_n is said to have *a valency of n*; the elements are classified as *uni-* (or *mono-*), *bi-* (or *di-*), *ter-* (or *tri-*), *quadri-* (or *tetra*) *valent*, etc., according as the value of n is one, two, three, four, etc.; or else they are called *monads*, *diads*, *triads*, *tetrads*, etc. Hydrogen forms the standard element, its valency being taken as unity.

The valencies of many elements cannot be determined from the preceding definition, owing to the fact that their hydrides are not known.[1] The conception of valency is therefore widened by regarding an element M as having a valency of n when it forms a compound with a halogen X[2] of the molecular formula MX_n. This extension is made in view of the fact that the halogens are univalent when compared with hydrogen, as seen in the preceding table. In the following table the chlorides (and one or two iodides and fluorides) of known molecular formulæ are given:—

LiCl	OCl_2	$SrCl_2$*	BCl_3	CCl_4	PF_5	SF_6	OsF_8
NaCl	$GlCl_2$	$BaCl_2$*	NCl_3	$SiCl_4$	AsF_5	SeF_6	
KCl	$CrCl_2$	$CdCl_2$*	PCl_3	$SeCl_4$	SbF_5	TeF_6	
KI	$FeCl_2$	$MnCl_2$*	$AsCl_3$	$TeCl_4$	$CbCl_5$	WCl_6	
RbCl	$ZnCl_2$	$CoCl_2$*	$SbCl_3$	$TiCl_4$	$TaCl_5$	WF_6	
CsCl	$GaCl_2$	$PdCl_2$*	$BiCl_3$	VCl_4	$MoCl_5$	MoF_6	
CsI	$SnCl_2$	$PtCl_2$*	$AlCl_3$	$GeCl_4$	WCl_5	UF_6	
InCl	$InCl_2$	$CuCl_2$*	$CrCl_3$	$SnCl_4$			
TlCl	$HgCl_2$		$FeCl_3$	$ZrCl_4$			
AgCl	$PbCl_2$		$GaCl_3$	UCl_4			
CuCl†	$CaCl_2$*		$InCl_3$				

* Molecular formula in solution in fused $BiCl_3$ (*vide* p. 117).

† Molecular formula in solution in fused $BiCl_3$. The molecular formula in the gaseous state is Cu_2Cl_2. All other formulæ in the table are derived from vapour-density measurements.

Only a few elements are excluded from both of the preceding tables. Of these, the inert gases form no compounds and hence exhibit no valency, and the valencies of the remaining elements are arrived at by assuming the simplest formulæ of their halides to represent the molecular formulæ in the absence of any definite evidence on the point.

The valency of an element, derived in the preceding manner, is regarded as indicating the number of other atoms with which one atom of the element can be directly united in a molecule. It is customary to indicate the valency of an element by a number of strokes radiating from the symbol of the element, and in this way *graphic* (*constitutional* or *structural*) *formulæ* are written, as indicated in the following examples:—

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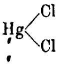
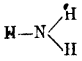
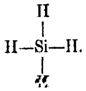
[1] Or, if known, are of unknown molecular weight In this case the simplest formula is assumed, *e.g.* NaH, CaH_2, etc.

[2] Fluorine chlorine bromine and iodine are the halogen elements.

$H-Cl$

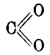


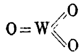




The conception of valency is still further widened. An atom of a diad element is capable of uniting with another diad atom to form a molecule, an atom of a tetrad with two diad atoms, and an atom of a hexad with three diad atoms; *e.g.* ZnO_1, CO_2, and WO_3 respectively.[1] In such substances,[2] which do not contain monad elements, the elements are still regarded as possessing their ordinary valencies and their graphic formulæ written

$Zn=O$





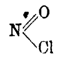
in accordance with this idea. An element with a valency of *n* is said to possess *n* valency bonds or linkages, and in the preceding cases oxygen is said to be united to zinc, carbon, and tungsten by two *valencies*, or two *bonds*, or two *units of affinity*; or else, united by a *double bond* (or *linkage*).

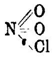
So far, binary compounds alone have been dealt with, and only those in which one atom of one element is united with one or more atoms of a second element. It will be seen that the valency of the first element is in these compounds given by the "rule"—

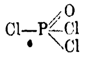
$$\text{valency} = \frac{\text{atomic weight}}{\text{chemical equivalent}},$$

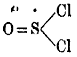
since the chemical equivalent of oxygen is chosen as one-half its atomic weight, and the hydride of oxygen is H_2O. The preceding rule is frequently stated as a definition of valency, but it is only of limited application.

From what has been already stated, the meanings attached to formulæ such, for example, as

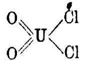




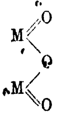


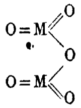


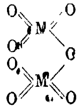
$O=C=S$



will be sufficiently clear. Various oxides of the types M_2O_3, M_2O_5, and M_2O_7 are regarded as having the constitutional formulæ





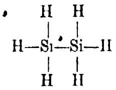


being oxides of triad, pentad, and heptad elements respectively. In the case of binary compounds, in which one element is a monad and more than one atom of the other is present in the molecule, it is naturally assumed that the polyvalent atoms are directly united to one another; *e.g.* silicon hydride Si_2H_6 is represented as

---

[1] The terms diad, tetrad, and hexad are here employed to denote valencies derived from a study of hydrides or halides.

[2] In the subsequent discussion molecular formulæ are often ascribed to substances although the molecular weights are not known; *cf.* footnote 1 on p. 283.



$$\begin{array}{c} \;\;\;\;\;\text{H}\;\;\text{H} \\ \;\;\;\;\;|\;\;\;\;| \\ \text{H—Si—Si—H} \\ \;\;\;\;\;|\;\;\;\;| \\ \;\;\;\;\;\text{H}\;\;\text{H} \end{array}$$

containing quadrivalent silicon, since in its hydride SiH_4, its halides SiX_4, and its oxide SiO_2, silica is quadrivalent. With compounds of this type, the "rule" for deducing valency does not give the accepted result; *e.g.* silicon would be a triad in Si_2H_6, in accordance with this method of deriving the valency.

It is possible to assign a valency to a radicle, or group of atoms that can be transferred as a whole from one molecule to another. The sulphate radicle (SO_4), for instance, is bivalent, since it combines with two atoms of hydrogen to form a molecule of sulphuric acid, H_2SO_4; and the hydroxyl radicle (OH) is univalent, as it unites with one atom of hydrogen to form water, H_2O.

Valency a Variable Property.—From the study of the hydrides the highest valency ever observed is *four*, *e.g.* silicon in SiH_4; from the halides *eight*, *e.g.* osmium in OsF_8; and from the oxides *eight*, *e.g.* osmium in OsO_4.

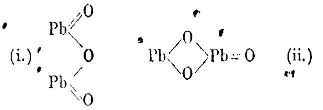
An element may exhibit more than one valency The following list of elements of variable valency is constructed from the data supplied by the two tables of formulæ previously given, and can be extended by considering the valencies deduced from the formulæ (empirical as a rule) of the oxides:—

Element.	Valency.	Element.	Valency.
Phosphorus	3 and 5	Tin	2 and 4
Arsenic	3 and 5	Uranium	4 and 6
Antimony	3 and 5	Molybdenum	5 and 6
Iron	2 and 3	Tungsten	5 and 6
Chromium	2 and 3	Sulphur	2 and 6
Gallium	2 and 3	Selenium	2, 4, and 6
Iridium	1, 2, and 3	Tellurium	2, 4, and 6

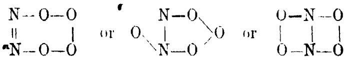
It is noteworthy how frequently the different values for the valency of an element differ by two, or a multiple of two.

Many attempts have been made to regard the valency of an atom as a fixed, invariable property, and, on this view of valency, to account for its apparently variable nature. This part of the subject will not, however, be discussed here. Most of the attempts are simply dialectical, amounting to little more than a restatement of plain, experimental facts in obscure and ill-defined terms; and in the absence of a satisfactory hypothesis as to the cause and nature of valency, they are of slight value.

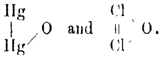
With some elements the assumption of a single value for the valency appears to be sufficient, *e.g.* calcium, bivalent in its hydride, chloride, and oxide. In regard to the other elements it is seldom necessary to assume a value other than one of those indicated from the compositions of the halides in order to arrive at structural formulæ for their compounds. The uncertainty attaching to these formulæ, however, must be frankly recognised. For example, lead appears to be bivalent in $PbCl_2$ and PbO, and quadrivalent in $PbCl_4$ and PbO_2, and hence is usually regarded as being either a diad or tetrad in all its compounds. Accordingly, the oxide Pb_2O_3 is not regarded as having the structure (i.) below, in which lead is represented as tervalent, but is represented by (ii.)—



Again, on the assumption that nitrogen is tervalent and oxygen bivalent, nitrogen peroxide N_2O_4 may be written



A similar indefiniteness attaches to the constitutions of many other substances, and the reasons adduced when selecting one of a number of alternative formulæ are often extremely flimsy. As a further example, the oxides M_2O are not all regarded as oxides of univalent elements. The favourite views concerning the constitution of mercurous oxide and chlorine monoxide, for instance, are those expressed by the formulæ



The difficulties and uncertainties encountered are attributable to the impossibility of at present defining va[illegible] definite manner, and the absence of a really satisfactory hypothes[illegible]s nature; and in this connection it should be mentioned that [illegible] not be confused with chemical affinity. The term *affinity* has, [illegible]equently been [illegible] used in discussions on valency.[1]

Valency and the Periodic Classifi[illegible].—Application [illegible] valencies that an element appears to exhibit, one [illegible] nea[illegible] express its group number in the Periodic Classificatio[illegible]s Groups 0 to VII. are concerned; *e.g.* aluminium, in Grou[illegible]ad, and tellurium, in Group VI., is sometimes a hexad.[2] This parti[illegible]lency may usually be assumed in an oxide, and, with the exception [illegible]value 7, in one at least of the halides. Thus, the valencies of the eleme[illegible]uld appear to vary periodically with their atomic weights, as was [illegible]ed out by Mendeléeff. Taking the elements of the second short series [illegible]ample,

Ne Na Mg Al Si P S Cl,

the valencies, derived from the oxides, are

0 1 2 3 4 5 6 7 . . . (A)

and from the halides,

0 1 2 3 4 5 6 7 . . . (B)

The hydrogen valencies, however, do not progressively increase, being in fact,

0 1 2 3 4 3 2 1 . . . (C)

---

[1] The valencies of the elements and the constitutional formulæ of their more important compounds are dealt with in Volumes II. to IX. of this series.

[2] The heptavalency of fluorine and bromine, and the hexavalency of oxygen, however, do not seem to be observed.

It is natural to suppose that the elements of Group VIII. may, on occasio exhibit a valency of eight, particularly now that an octafluoride of osmiu is known; and osmium and ruthenium are accordingly regarded as octad in the oxides OsO_4 and RuO_4. Evidence for the octavalency of the othe transitional elements is, however, lacking.

The values for the valencies of the elements derived on the assumptio that valency is periodic, are not always the values commonly exhibited b the elements, *e.g.* thallium, lead, bismuth, etc. It is noteworthy, however that the values thus derived represent, with very few exceptions (*e.g.* copper gold), the *maximum* valencies of the elements. Hence it is that althoug an element may usually exhibit one particular valency, higher valencies ar often assumed in order to account for the existence of certain compounds Higher valencies than *one* are, for example, often assumed in the case of th halogens in order to "explain" the existence of double salts, such compound as ICl_3, IF_5, etc., the assumptions being justified by reference to the Periodi Classification, which indicates a maximum valency of *seven* for the halogens.

Theory of Valency.—The various theories of valency that have bee suggested from time to time fall broadly speaking into two groups, namel *chemical* and *physical*. The former content themselves with postulating th existence of certain definite or indefinite attractive forces, and proceed to discussion of the internal structures of various *molecular* chemical entities whilst physical theories concern themselves primarily with the nature those attractive forces and the constitution of the *atoms*. It is important t bear this distinction in mind, "because it is then obvious that chemica theories of valency do not necessarily stand or fall with the physical; on th contrary, they may and often do admit of interpretation according to th different views on matter that physical science from time to time suggests."[1]

A.—Chemical Theories of Valency.

Abegg's Theory[2] attributes two kinds of valency of opposite polarit to every element, namely *normal* and *contra*. Of these the former is th more active and corresponds to the recognised valency of the elements, whils the latter explains their so-called residual affinities. When its norma valencies are positive in character the element possesses the properties of metal, whilst the normal valencies of non-metals are negative. The arith metical sum total of normal and contra-valencies for each element is eight, and their relative distribution determines the position of the element in th periodic table. Thus:

Horizontal groups	1	2	3	4	5	6	7
Typical elements	Li	Gl	B	C	N	O	F
Normal valencies	+ 1	+ 2	+ 3	+ 4	− 3	− 2	− 1
Contra valencies	− 7	− 6	− 5	− 4	+ 5	+ 6	+ 7

A little consideration will show that this theory affords a ready explanatio for association, for the formation of molecular compounds such as double salts and the like. It also serves to explain the amphoteric nature of nitrogen carbon, etc., which combine readily with electropositive hydrogen and ye yield very stable compounds with electronegative oxygen.

---

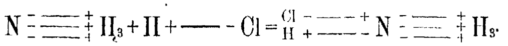
[1] Friend, *The Theory of Valency* (Longmans & Co. Second Edition, 1915), p. 170.

[2] Abegg and Bodlander, *Zeitsch. anorg. Chem.*, 1899, **20**, 453; Abegg, *ibid.*, 1904 **39**, 330.

[3] For a physical interpretation of this see Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 762.

Both Spiegel[1] and Arrhenius[2] have suggested that certain elements possess, in addition to their ordinary valencies, *neutral affinities* (Spiegel) or *electrical double valencies* (Arrhenius), which are simply ordinary valency bonds capable of being utilised in pairs of equal and opposite sign. When not in use they neutralise each other within the atom, and consequently do not affect the electrochemical nature of the latter. Friend[3] has still further developed these views and applied them to the study of complex salts for which he suggests cyclic formulæ in preference to the co-ordinated structures of Werner.

As illustrative of the manner in which the latent or neutral affinities act the combination of ammonia with hydrogen chloride may be taken In NH_3 the nitrogen atom is tervalent, and no compound of the type NH_5 appears capable of existence. The maximum free negative valency of nitrogen is thus seen to be three. In ammonium chloride, however, the nitrogen has a valency of five, a pair of latent or neutral affinities having been called out by the additional atoms of hydrogen and chlorine. Thus



$$\mathrm{N}\begin{array}{c}-\text{———}+\\-\text{———}+\\-\text{———}+\end{array}\mathrm{H}_3+\mathrm{H}+\text{———}-\mathrm{Cl}=\begin{array}{c}\mathrm{Cl}\\\mathrm{H}\end{array}\begin{array}{c}-\text{———}+\\+\text{———}-\end{array}\mathrm{N}\begin{array}{c}-\text{———}+\\-\text{———}+\\-\text{———}+\end{array}\mathrm{H}_3.$$

As will be seen later, all of these theories are capable of an electronic interpretation which harmonises them with the most recent views on the constitution of the atom. Two other theories of importance remain to be mentioned, namely the **crystallographic theory** of Barlow and Pope and the **co-ordination theory** of Werner. The former has already been discussed (pp. 75–78), and its inadequacy has recently been shown by Richards[4] and by Barker,[5] the latter having subjected it to severe and rigid criticism.

The theory of Werner,[6] originated in 1893, has been widely accepted, and has proved very useful in its application to the study of complex salts such as the metalammines. Originally two kinds of valency were postulated, namely *Principal* and *Auxiliary*. The former were the ordinary valencies of the elements, whilst the latter were additional valency bonds which could come into play when the ordinary valencies of an element were saturated. For example, ammonia and hydrogen chloride are saturated compounds. Union to form ammonium chloride was supposed to take place by an auxiliary valence, represented by the broken line

$$H_3N\;.\;.\;.\;HCl.$$

It has now been concluded, however, that the differences originally assumed between principal and auxiliary valencies do not really exist;[7] hence the above scheme tacitly assumes that nitrogen has a valency of four, whilst one hydrogen atom has a valency of two. This is opposed to our ordinary conception of valency, although that in itself does not necessarily prove that Werner is wrong, for the recognition of valency bonds at all is admittedly an arbitrary assumption. The formula, however, has nothing in particular to recommend it, whilst many objections may be raised against it.

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[1] Spiegel, *Zeitsch. anorg Chem.*, 1902, **29**, 365.

[2] Arrhenius, *Theorien der Chemie*, Leipzig, 1906.

[3] Friend, *Trans. Chem. Soc.*, 1908, **93**, 260, 1006 ; 1916, **109**, 715.

[4] Richards, *J. Amer. Chem. Soc.*, 1913, **35**, 381 ; 1914, **36**, 1386. See Barlow and Pope, *ibid.*, 1914, **36**, 1675, 1694.

[5] Barker, *Trans. Chem. Soc.*, 1912, **101**, 2484 ; 1915, **107**, 744.

[6] Werner gives a very complete account of his views in *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*, Brunswick, 1913.

[7] Werner, *Ber.*, 1913, **46**, 3674. Dubsky, *J. prakt. Chem.*, 1914, [ii.], **90**, 61.

Werner's theory, however, affords a useful method of classifying complex salts, and to it we owe the discovery of the asymmetric cobalt atom. From this point of view it is discussed in Volume IX. in connection with the metalammines.

B.—Physical Theories of Valency.

A theory attempting to explain the actual cause of valency must of necessity be influenced by the views held at the time of its promulgation on the constitution of matter in general and on the structure of the atom in particular. When atoms were regarded as hard, impenetrable spheres the suggestion that they possessed hooks enabling them to cling to each other was a perfectly reasonable one. Such an hypothesis, however, is entirely out of the question if modern conceptions of the electrical nature of chemical forces are accepted.

The close connection between electricity and chemical affinity has been made the subject of observation for very many years: both Davy[1] and Berzelius[2] regarded chemical combination as essentially an electrical phenomenon. Blomstrand[3] in 1869 drew attention to the fact that the smallest number of valency bonds is possessed by those elements which exhibit the most decided electrochemical character. Thus the alkali metals and the halogens are highly electropositive and negative respectively, and their valency is unity. Carbon, on the other hand, is amphoteric, and its valency is four.

Helmholtz[4] in 1881 again drew attention to the electrical nature of chemical force. The laws of electrolysis (Faraday's Laws, p. 202) naturally suggest that electricity is of an "atomic" nature, since the atom of an element of valency *n* must be supposed to carry *n* times the quantity of electricity that a univalent atom carries. According to Helmholtz, each "unit of affinity" that an atom is said to possess represents a charge of what might be termed one "atom of electricity," positive or negative as the case may be.

Since Helmholtz propounded his views the electrical theory of valency has received an increasing amount of attention.[5] According to modern physical theory, the "atoms of electricity" are capable of existing apart from matter, the "cathode rays" shot off from the cathode when an electric current is passed through a rarefied gas consisting of streams of these electrical atoms or *electrons*. An electron is a *negative* electrical charge, identical with the charge associated in electrolysis with the atom of a univalent electronegative element, *e.g.* chlorine.

The modern view of the structure of the atom has already been briefly outlined (p. 276). An atom is regarded as consisting of a positively charged nucleus surrounded by the requisite number of negative electrons to render the atom electrically neutral. Some of these electrons are mobile. Most scientists who have discussed the subject follow the view propounded by J. J. Thomson in 1904, namely, that mobile electrons may be detached from one atom and transferred to another. On this view, a positive (or negative) ion is an atom that has lost (or gained) one or more electrons; whilst the different valencies of the elements and their chemical and electrochemical characters depend upon the manner in which the stabilities of the electron systems constituting their neutral atoms are affected by the loss or gain of electrons. Combination between atoms represents a transference of electrons from some atoms to others. For each valency bond established between two atoms the transference of one electron takes place, the losing atom acquiring a unit positive charge and the receiving atom a unit negative charge of electricity.[1]

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[1] Davy, *Phil. Trans.*, 1807, 97, 1.

[2] Berzelius, *Lehrbuch der Chemie* (Dresden, 2nd edn., 1827), iii., Part I. See this volume, p. 193.

[3] Blomstrand, *Chemie der Jetztzeit*, 1869, pp. 217, 243.

[4] Helmholtz, *Trans. Chem. Soc.*, 1881, 39, 277.

[5] See, *e.g.*, Lodge, *Modern Views on Matter*, The Romanes Lecture, 1903; *Nature*, 1904, 70, 176; P. F. Frankland, *Nature*, 1904, 70, 223, and the references cited in succeeding footnotes.

The preceding electronic conception of valency gives a satisfactory explanation of highly reactive compounds, *e.g.* many inorganic compounds, but difficulties are encountered in applying it to most organic compounds.[2] Moreover, since the inception of the preceding theory of valency the developments of physical science have led to the conclusion that it cannot be of universal validity, since it necessitates the atoms in a molecule being positively or negatively charged, and there is clear evidence that in certain molecules the atoms are electrically neutral.[3] In part, this evidence is supplied by Thomson's "positive ray" method of analysis,[4] and Thomson has changed his opinion regarding the mechanism of the attraction between atoms. He now considers[5] that the electrical forces which keep the atoms in a molecule together are due not to some atoms being charged positively and others negatively, but to the displacement of the positive and negative electricity in each atom. Each atom thus acts like an electrical doublet, and attracts another atom in much the same way that two magnets attract each other. As in the earlier theory, mobile electrons are supposed to exist in atoms, but, in chemical combination between atoms, the electrons belonging to a particular atom are held by such constraints that, although they move from their normal positions, it is the exception and not the rule for them to leave the atom and transfer themselves to another atom (or atoms). The number of mobile electrons in the neutral atom of an element is supposed to be identical with the number of the vertical group in the Periodic Table in which the element finds a place. Thus, hydrogen and the alkali metals in the first group possess one such electron, and so on.

A mobile electron in an uncombined atom is connected to the nucleus by a tube of force. When combination takes place with a second atom this tube of force is regarded by Thomson as becoming anchored on to the nucleus of the second atom. If both atoms are to remain neutral, clearly the positive end of one mobile electron of the second atom must migrate to the nucleus of the first atom. Thus each valency bond is represented by two tubes of force, and when each mobile electron in an atom has been accounted for in this way the atom is saturated and exerts its maximum valency.

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[1] J. J. Thomson, *Phil. Mag.*, 1904, [vi.], **7**, 237 ; 1906, [vi.], **11**, 769 ; *Electricity and Matter* (Constable, 1904) ; *The Corpuscular Theory of Matter* (Constable, 1907). Ramsay, *Trans. Chem. Soc.*, 1908, **93**, 778. Falk and Nelson, *J. Amer. Chem. Soc.*, 1910, **32**, 1637 ; Falk, *ibid.*, 1911, **33**, 1140 ; 1912, **34**, 1041 ; Nelson, Beans, and Falk, *ibid.*, 1913, **35**, 1810 ; Falk and Nelson, *ibid.*, 1914, **36**, 209 ; 1915, **37**, 274. Fry, *ibid.*, 1908, **30**, 34 ; 1912, **34**, 664 ; 1914, **36**, 248, 262, 1035 ; 1915, **37**, 855 ; *Zeitsch. physikal. Chem.*, 1911, **76**, 385, 398, 591 ; 1912, **80**, 29 ; 1913, **82**, 665. Guthrie, *J. Roy. Soc. N.S. Wales*, 1912, **45**, 318. W. A. Noyes, *J. Amer. Chem. Soc.*, 1913, **35**, 767.

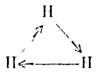
[2] See, *e.g.*, the criticism of the theory by Brunel, *J. Amer. Chem. Soc.*, 1915, **37**, 709.

[3] For a summary of the physical objections to the theory, see Bates, *J. Amer. Chem. Soc.*, 1914, **36**, 789.

[4] J. J. Thomson, *Rays of Positive Electricity* (Longmans & Co., 1913) ; *Phil. Mag.*, 1907, [vi.], **13**, 561 ; 1909, **18**, 821 ; 1910, **20**, 752 ; 1911, **21**, 225 ; 1912, **24**, 209, 668.

[5] Sir J. J. Thomson, *Phil. Mag.*, 1914, [vi.], **27**, 757.

If these views are accepted, it is possible to write valency formulæ for many molecules when it is impossible to do so on the ordinary views of valency. For example, it is possible to formulate a molecule H_3; for if, in the accompanying figure, H denotes an atom of hydrogen and the arrow the direction of a tube of force from an atomic nucleus to an electron, it is clear that each atom is represented as containing only one mobile electron, and is also electrically neutral since it is the origin of one and the termination of another tube of force:—



Lewis[1] has outlined an attractive electronic theory of chemical combination which is in many respects similar to Thomson's later theory, but which postulates that in chemical combination between two atoms a mobile electron may be common to both atoms.[2] Finally, reference may be made to the valency theory of Stark, which, since it was published in 1908, has been applied with considerable success to the interpretation of chemical phenomena.[3] Stark's theory, like the theories of Thomson and Lewis, is electronic in character, and also avoids the assumption that electrons are transferred from some atoms to others in chemical combination.

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[1] Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 762; *cf.* Lewis, *ibid.*, 1913, **35**, 1418; Bray and Branch, *ibid.*, 1913, **35**, 1140.

[2] Compare the electronic theory developed by Arsem, *J. Amer. Chem. Soc.*, 1914, **36**, 1655.

[3] J. Stark, *Jahrb. Radioaktiv. Elektronik.*, 1908, **5**, 125. See Ruggli, *Die Valenzhypothese von J. Stark vom chemischen Standpunkt* (Stuttgart, 1912), and for a summary, see Miss A. Hahn and Miss M. E. Holmes, *J. Amer. Chem. Soc.*, 1915, **37**, 2611.

VOLUME I. PART II.

THE INERT GASES

BY

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PART II.—THE INERT GASES.

CHAPTER I.

INTRODUCTION.

THE purpose of this Part is to give an account of a remarkable family of gaseous elements, sharply characterised and distinguished from all other families of elements by their chemical inactivity. For this reason they are spoken of generally as the "inert gases," or sometimes, by analogy with gold and platinum, as the "noble gases."

Perusal of the detailed history of these gases will reveal how very largely we owe our knowledge of them to the labours of Sir William Ramsay and his collaborators. Helium was, by many years, the first to be discovered; but it was then known only as a substance present in the solar atmosphere. Later, certain observations by Rayleigh on the density of atmospheric nitrogen directed attention to Cavendish's experiments on air, and a repetition of his work led to the discovery of argon. A thorough search for new sources of this gas led to the further discovery that certain rare minerals contained quite considerable amounts of helium.

With the perfection of apparatus for the liquefaction of air by the process of self-intensive refrigeration, it became possible to liquefy and fractionally distil quantities of atmospheric argon, and in the heavier fractions of this gas Ramsay and Travers found the new inert gas krypton. Application of the same methods to still larger quantities of argon led to the discovery of neon with helium in the lighter fractions; and of xenon with krypton in the heavier fractions.

The historical sections of the subsequent chapters, if taken together in the order indicated above, will give some idea of a story as interesting, perhaps, as any that can be found in chemical literature.[1]

With the exception of argon, these gases are present in air in extremely minute amounts, hence they are frequently spoken of as the "rare gases."

It was at first suggested that argon might be a polymer of nitrogen, related to that gas just as ozone is to oxygen; and that helium might similarly be a polymer of hydrogen. But a gas of the molecular formula N_3 would have a density of 21, whereas the density of argon is under 20; and a similar discrepancy is found in the case of helium. With the discovery of the other gases of the group, the polymerisation theory was finally abandoned.

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[1] See Ramsay, *The Gases of the Atmosphere* (Macmillan & Co., 1902); and Moore, *Chem. News*, **1911**, **103**, 242.

It follows, then, that these gases must be either compounds of known elements—a very unlikely thing in view of their extreme indifference to all chemical agents—or else new elementary substances. It is now generally believed that the latter alternative is correct, and the positive evidence for this belief may be briefly summarised here:—

1. The inert gases give very characteristic spectra, which, nevertheless, show general resemblances. For example, all give dual spectra.

2. They are chemically inert (see pp. 320, 342).

3. They show general resemblances and gradations in physical properties such as are seen in other families or groups of elements. This can be readily seen by referring to Table I., in which the physical constants of the various gases are tabulated.

TABLE I.[1]

	Helium	Neon.	Argon	Krypton	Xenon	Niton.
Colour	None	None	None	None	None	None
Smell: Taste	None		None			.
Ratio of sp. heats, γ	1·652	1·642	1·65	1·689	1·666	.
Weight in grams of normal litre	0·1786	0·9002	1·7818	3·708	5·851	9·97
Density (O = 16)	1·999	10·100	19·94	41·506	65·35	111·5
Mol. wt. = At. wt.	4·00	20·20	39·88	82·92	130·2	222·4
Thermal conductivity $\kappa \times 10^6$	33·86	109·1	38·94		.	
Refractivity: $(\mu - 1) \times 10^6$ for λ 5461	34·925	67·16	282·0	428·74	705·49	.
Dispersion: $C \times 10^{-27}$ in Sellmeier equation	2·425	5·187	9·433	10·689	12·242	..
Critical temperature	5° abs	60° abs	150°·6 abs	210°·5 abs	289·6 abs	377°·5 abs
Critical pressure	2·75 atmo	29 atmo	47·996 atmo	54·3 atmo	58·2 atmo	62·5 atmo
Boiling point	4°·5 abs	27·1 abs	86° abs	121·2 abs	163·9 abs	211 abs
Melting-point	..		83°·4 abs	104° abs	133 abs	202° abs
Vapour-pressure ratio			0·0350	0·0167	0·0675	.
Density of liquid at boiling-point	0·151		1·4046	2·155	3·06	5 (approx.)
Compressibility	Zero	−0·00105	+0·00081	+0·00210	+0·00690	..
Solubility in water: Absorption coefft. at 0°	0·0134	0·0114	0·0561	0·1207	0·2189	0·5
Viscosity, at 0°: C.G.S. units × 10⁴	1·879	2·981	2·102	2·334	2·107	.
Temperature coefft. of viscosity: $\beta \times 10^5$	232	22	283	308	339	.

From this table it will be observed that all these gases are colourless, and probably all are odourless and tasteless, and that in every case the ratio of

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[1] By *compressibility* in this table is understood the coefficient A_0^1 defined in this Vol., Part I., p. 131; it refers to 0° C. The values for helium and neon are the results of direct measurements, the others have been obtained indirectly by comparing Guye's "critical constants" equations (Part I., p. 135) with Berthelot's "limiting density" equation (Part I., p. 133), and assuming the necessary critical data. The molecular and atomic weights given are those obtained by the method of critical constants (Ar, Kr, Xe) or the method of limiting densities (He, Ne).

By *vapour-pressure ratio* is meant the value of *c* in the equation

$$T_a/T_b = T_{a'}/T_{b'} - c(T_a - T_{a'}),$$

where T_a, $T_{a'}$ are the temperatures (abs.) at which the inert gas has the vapour pressures p_1 and p_2, and T_b and $T_{b'}$ are the temperatures at which methyl alcohol has the same vapour pressures p_1 and p_2 respectively.

For the *molecular velocities*, *molecular diameters*, and *mean free paths*, and also the *refractive indices* of the liquefied gases, see Rudorf, *Phil. Mag.*, 1909, [vi.], 17, 795.

the specific heats approximates closely to the theoretical value (1·667) for a monatomic gas.

Although the data in some cases are incomplete, a uniform gradation of properties is clearly seen in the values of the density and molecular weight, the thermal conductivity, the refractive index and dispersion, the critical temperature, the boiling-point and melting-point, the density of the liquid, and the vapour-pressure ratio. With reference to the compressibility, the solubility in water, the viscosity, and the specific inductive capacity, it will be observed that there is a similar gradation of properties, the uniformity of which is, however, broken in the case of neon. Why this should be so is not at all obvious, but it may be remarked that the compressibility, the solubility, and the viscosity are known to be dependent upon the attraction between the molecules, and it seems therefore that, while from their relations of their critical temperatures one would expect neon to be less "perfect" than helium, in reality it is "ultraperfect" at ordinary temperatures.

It will be evident from even a casual glance at the table that the similarities and gradations of properties mentioned above do undoubtedly exist, but no simple and exact numerical relationship has been traced. This is quite in accordance with what we observe in other families of elements, but, it, nevertheless, represents the grave of a buried hope. When argon and its companions were first found to have such a simple molecular structure, it was thought that the study of their properties might give some clue to the riddle of the periodic table, but hitherto it has not been possible to find any mathematical expression which will enable us to calculate accurately the value of even one constant of one gas from the values determined for others.[1]

It has been already mentioned that the ratio of the specific heats indicates that each of the inert gases is monatomic. Perhaps the most convincing evidence of the truth of this conclusion is afforded by the results of J. J. Thomson's researches on rays of positive electricity.[2] Other evidence bearing on the atomicities of these gases is given in the subsequent chapters.[3]

It will now be evident that this family of inert gases should find a place in the Periodic Classification. The table as usually written before their discovery (see Frontispiece, Part I, omitting Group 0), appeared to be complete, except for occasional gaps into which they could not, by any possibility, be fitted.

Now if we consider the atomic weights of the first three members of the argon group, it is evident that they can find a place only in the eighth group, or by themselves in a new group preceding Group I. The former alternative was strongly upheld in the earlier days of their discovery, but the latter position was preferred by the discoverers and is now generally accorded to these gases.

Usually the position of an element in the table can be justified by referring to its chemical behaviour as compared with that of neighbouring elements; and it might at first sight appear that this kind of reasoning was inapplicable to the inert gases. This inertness, however, affords the strongest possible justification for placing them in Group 0, as may be readily seen if we remember that the above table is only a convenient way of expressing the fact that if we pass from lithium through boron, carbon, nitrogen, oxygen, and fluorine to sodium, we find in the last element a modified reproduction of the properties of the first. This is most conveniently illustrated by one of the various spiral arrangements of the table which have been proposed from time to time.[1]

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[1] Approximate relations have been discovered; see, *e.g.*, Loring, *Chem. News*, 1911, **103**, 71.

[2] Sir J. J. Thomson, *Rays of Positive Electricity* (Longmans & Co., 1913).

[3] For a discussion of the atomicities of the inert gases, see H. E. Armstrong, *Science Progress*, 1913, **7**, 648; Sir O. Lodge, *ibid.*, 1913, **8**, 197; Soddy, *ibid.*, 1914, **8**, 654.

It is then evident that it is immaterial whether the new group is placed before the first or after the eighth group:[2] it is in either case a transitional group through which we pass from the extremely electronegative halogens to the other extreme—the electropositive alkali metals. The characteristics to be expected in such transitional elements were indicated by Julius Thomsen by a mathematical analogy. The change of periodic functions from + to − values can only take place by passage through zero or infinity: the first mode is *gradual* and corresponds to the change of properties observed as we pass along a series; the second is *abrupt* and corresponds to the change involved in passing from one series to the next.

According to Thomsen, it was probable that the transition from one series to the next should take place *via* an element, the electrical character of which corresponded to ±∞, and that the valency of such an element would be *zero*; accordingly he supposed that there should be interposed between the series a group of elements of *zero* valency, electrically and chemically indifferent. Thomsen, indeed, predicted the discovery of a group of such elements whose atomic weights should be 4, 20, 36, 84, 132, and 212.[3]

It may be mentioned here that a protest was, at one time, entered against altering the periodic table in order to make a place for these gases,[4] and it is perhaps a trifle Gilbertian to devote a section of a text book on chemistry to elements devoid of chemical properties. Nevertheless, the relationships indicated above provide a sufficient justification for so doing, and indeed show that without the inert gases the periodic system would be incomplete. In view of Mendeléeff's suggestion that a member of the group lighter than hydrogen might exist, it is appropriate to mention here that a search for such a gas in air has proved fruitless;[5] and also it may be added that if there is any other inert gas of high atomic weight present in the atmosphere, the amount of that gas must be extremely small in comparison with the amounts of krypton and xenon present.[6]

The only difficulty that arises in placing Group 0 between Group I. and Group VIII. is that it brings argon between chlorine and potassium, an arrangement which is *not* in accordance with their atomic weights, as the following table shows:—

...	He = 4·00	Li = 6·94
F = 19·0	Ne = 20·20	Na = 23·00
Cl = 35·46	A = 39·88	K = 39·10
Br = 79·92	Kr = 82·92	Rb = 85·45
I = 126·92	Xe = 130·2	Cs = 132·81
...	Nt = 222·4	...

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[1] See this volume, Part I. Chap. VIII.

[2] See, *e.g.*, Howe, *Chem. News*, 1899, 80, 74.

[3] J. Thomsen, *Zeitsch. anorg. Chem.*, 1895, 9, 283.

[4] Piccini, *Zeitsch. anorg. Chem.*, 1899, 19, 295; *Gazzetta*, 1899, 29, 169: *cf.* Martin, *Proc. Chem. Soc.*, 1901, 17, 259.

[5] Coates, *Proc. Roy. Soc.*, 1907, 78, 479.

[6] See Sir J. J. Thomson, *Rays of Positive Electricity* (Longmans & Co., 1913), p. 111.

It is not possible to explain why the atomic weight of argon is greater than that of potassium: one can only point to other similar cases—*e.g.* iodine and tellurium, cobalt and nickel—and say that in this case, as in those, the evidence of chemical relationship appears to justify a violation of the order of atomic weights.

In order that Group 0 may be strictly analogous to the other groups, it should contain a typical element and odd and even subgroups. If this is really the case, then the only representative of the odd subgroup at present known is neon. It has been already noted that neon differs in several respects from the other known members of the group.

Much interest has been aroused by the discovery that the α-rays of radioactive elements consist of material particles which are atoms of helium carrying two atomic charges of electricity; and that niton, the first product of the disintegration of the radium atom, is a member of this group. It seems practically certain, too, that krypton, though present in the air in most minute accounts, is largely responsible for the splendour of the *aurora borealis*. These matters, and many other interesting points in connection with the rare gases, are dealt with more fully later.

CHAPTER II.

HELIUM (He).

History.—During the solar eclipse visible in India on the 18th August 1868, a spectroscope was for the first time turned upon the solar chromosphere—the luminous atmosphere of gas which surrounds the sun. Many observers noticed in the chromospheric spectrum a yellow line, supposed by them to be the D lines of sodium. Janssen pointed out[1] that this line did not exactly coincide with the sodium lines D_1 and D_2, and he proposed to call it D_3. Shortly afterwards, Frankland and Lockyer[2] came to the conclusion that this line could not be attributed to any known terrestrial substance, but must be due to a new element existing in the sun. To this hypothetical element they gave the name *helium* (Gr. ἥλιος, the sun); a name which was generally accepted by astronomers to denote the substance giving rise to the line D_3. As observations accumulated, certain other lines were seen always to accompany this line and to vary with it in intensity, and they were consequently attributed to the same source. The chief of these were λ7056 λ4472, and λ3970;[3] D_3 itself has λ5876.

Until the year 1895 the only reference to the possible existence of terrestrial helium is found in a note by the astronomer Palmieri,[4] who observed that a lava-like product from Vesuvius gave a yellow spectral line of wave-length λ = 5875, and concluded that it contained helium. Unfortunately no details of his method of experiment are given, and it is possible that his observation was mistaken. Helium is known to occur in Vesuvian minerals,[5] but it is not possible to obtain the helium spectrum from helium minerals either by heating in the flame or by the spark.[6]

The actual discovery of terrestrial helium was made by Sir William (then Professor) Ramsay in the latter part of 1894 when searching for new sources of argon, then recently discovered. While engaged in this investigation he received a letter from Miers, the eminent mineralogist at that time connected with the British Museum, in which it was suggested that it might be worth while to examine certain uraninites (varieties of pitch-blende) from which Hillebrand[7] had obtained a gas which he had supposed to be nitrogen. Ramsay considered it improbable that nitrogen could have been obtained from its compounds by the methods Hillebrand had used, and therefore proceeded to re-examine clèveite, one of the minerals from which the supposed "nitrogen" had been obtained.

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[1] Janssen, *Compt. rend.*, 1868, 67, 838.

[2] Frankland and Lockyer, *Proc. Roy. Soc.*, 1868, 17, 91.

[3] Landauer, *Spectralanalyse* (1869), p. 155.

[4] Palmieri, *Rendiconti R. Accad. di Napoli*, 1881, 20, 233.

[5] Piutti, *Le Radium*, 1910, 7, 142.

[6] Nasini and Anderlini, *Atti R. Accad. Lincei*, 1904, [v.], 13, i. 368.

[7] Hillebrand, *Bull. U.S. Geol. Survey*, 1889, No. 78, 43.

It was really a most unfortunate chapter of accidents that prevented Hillebrand from making the discovery of helium. He had confirmed the presence of nitrogen in the clèveite gas in various ways: (*a*) the gas when sparked with oxygen gave nitrous fumes, (*b*) sparked with hydrogen in presence of hydrochloric acid it gave ammonium chloride, the identity of which was proved by conversion into ammonium platinichloride and estimation of platinum in that salt; (*c*) when subjected to an electrical discharge in a vacuum tube the gas gave a strong nitrogen spectrum. Ramsay was able to confirm the accuracy of these results, as he found about 12 per cent. of nitrogen in the helium from clèveite.

Hillebrand, writing to Ramsay after the discovery of helium had been announced, explained that he had noticed that in his experiments the formation of nitrous fumes and ammonia proceeded very slowly, and that the spectrum contained many lines not attributable to nitrogen. To the first phenomenon he attached but little significance as he was using only a small current. He was aware that the spectra of gases are profoundly influenced by changes of pressure, and therefore, though he and his assistant jocularly suggested that they might be dealing with a new element, the matter was allowed to drop, and helium remained undiscovered for another five years. Truly a great discovery narrowly missed!

Ramsay heated powdered clèveite with dilute sulphuric acid, sparked the resulting gas with oxygen over soda, removed excess of oxygen with alkaline pyrogallate, washed with water, dried, and transferred to a vacuum tube. The light given by the passage of electricity through this tube was examined visually in a spectroscope alongside that from a Plücker tube containing argon, as a comparison. It so happened that this second tube, owing to impurities contained in the magnesium electrodes, gave the spectra of hydrogen and nitrogen as well as the argon spectrum. It was at once evident that the clèveite gas contained some argon and hydrogen, but it gave also a brilliant line in the yellow, nearly, but not quite, coincident with the yellow sodium lines.

The wave-length of this line was measured by Crookes and proved to be exactly that of the solar D_3 line. It thus became known that helium could thenceforward be reckoned among the number of terrestrial elements.[1]

This discovery was quickly confirmed by Clève[2] and by Lockyer, who prepared a sample of the new gas from broggerite, and identified in its spectrum many lines which had previously been attributed to helium.[3]

Before long doubt was cast both on the elementary nature of the gas and on its identity with solar helium. Runge and Paschen showed that the spectrum lines of helium fell naturally into six series which were related to one another in sets of three. In each set there was a Principal Series composed of strong lines, and two Subordinate Series, consisting of weaker lines, which converged to a common limit. The series showed general resemblances to the series of hydrogen, on the one hand, and to that of lithium on the other. Moreover, when the gas was allowed to stream through a porous plug into a Plücker tube, the light at first was green, the line λ5016 of the single line group being equal in intensity to D_3, and then gradually became yellow as D_3 became relatively stronger.[1] This observation was confirmed by Brauner.[2] These investigators therefore concluded that they had separated clèveite gas into two components: helium of density 2·2, and a lighter gas for which a name, *parhelium*, was actually proposed. This view received some support from the fact that helium from different minerals showed considerable variations in density (from 2·181 to 2·114),[3] and by diffusion through porous earthenware could be separated into two fractions differing still more in density. It was even suggested that there might be two sizes of molecules in the gas.[4]

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[1] Crookes, *Proc. Roy. Soc.*, 1895, 58, 69.

[2] Clève, *Compt. rend.*, 1895, 120, 834 and 1212.

[3] Lockyer, *Proc. Roy. Soc.*, 1895, 58, 69.

The homogeneity of helium was subsequently proved in two ways. Travers[5] showed that on passing an electrical discharge through helium contained in a vacuum tube with platinum electrodes the pressure fell steadily, owing to the absorption of the gas by the finely divided platinum deposited on the walls of the tube, and that with this fall in pressure the colour of the glow changed from orange-yellow, through bright yellow and yellowish-green, to green. At this point the tube was allowed to cool, the residual gas was pumped out, and the tube was heated with a flame in order to drive out the gas occluded in the platinum. According to the hypothesis advanced by Runge and Paschen, this gas should have contained an excess of that constituent to which the yellow line of helium was due, but when the discharge was again passed through the tube it showed exactly the same behaviour as the original gas.

Further, Ramsay and Travers[6] conducted an exhaustive fractional diffusion of clèveite gas and found that, though it could certainly be separated into two portions of densities 1·979 and 2·245 respectively, the lighter fraction, which possessed all the properties attributed to helium, was *unchanged* by further diffusion, while the heavier portion under this treatment gave still heavier fractions which were ultimately shown by spectroscopic observation to contain argon. The uncertainty caused by the differing densities of natural helium was thus satisfactorily removed and the elementary nature of the new gas demonstrated.

At one stage of its history the identity of clèveite gas with solar helium was also open to doubt as the former gave a yellow line which was undoubtedly double,[7] while the solar line D_3 had not, at that time, been resolved.[8] Later, however, both Huggins[9] and Hale[10] showed that the solar line was also double.

During the first year following the discovery of helium—argon being the only member of the group then known—its position in the periodic classification was matter for much discussion,[11] and even as late as 1899 Brauner[12] showed considerable ingenuity in devising reasons for considering helium and argon to be inert compounds or allotropic modifications of known elements. With wider knowledge of the group to which helium belongs it becomes, however, increasingly probable that the commonly accepted views as to its elementary nature and position in the periodic classification are correct.

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[1] Runge and Paschen, *Phil. Mag.*, 1895, [v.], **40**, 297

[2] Brauner, *Chem. News*, 1896, **74**, 223. [3] Ramsay, *Proc. Roy. Soc.*, 1896, **59**, 325.

[4] Ramsay and Collie. *Proc. Roy. Soc.*, 1896, **60**, 206.

[5] Travers, *Proc. Roy. Soc.*, 1897, **60**, 449.

[6] Ramsay and Travers, *Proc. Roy. Soc.*, 1897, **60**, 206; 1898, **62**, 316.

[7] Runge, *Nature*, 1895, **71**, 283.

[8] Huggins, *Chem. News*, 1895, **71**, 283; Bélopolsky, *Mem. Societá Spett. Ital.*, May 1894

[9] Huggins, *Chem. News*, 1895, **72**, 27.

[10] Hale, *Astronom. Nachrichten*, 1895, **138**, 227.

[11] See, *e.g.*, Deeley, *Chem. News*, 1895, **72**, 297; Wilde, *Phil. Mag.*, 1895, [v.], **40**, 466.

[12] Brauner, *Ber.*, 1899, **32**, 708.

Up to 1903 the work done on helium consisted mainly in the detailed examination of its properties, but in that year Ramsay and Soddy[1] made the sensational discovery that this gas was a product of the atomic disintegration of radium. This discovery will be dealt with more fully later; it is merely necessary to state here that it has been shown since that helium is also produced in the disintegration of other radioactive elements, and that the atom of helium is identical with the α particle.

It has been supposed that helium can be produced by the passage of an electrical discharge through hydrogen (*see* Neon, p. 323). Sir J. J. Thomson has obtained evidence by his positive-ray method of the continuous evolution of helium from salts by the action of cathode rays.[2]

After many fruitless attempts to liquefy helium had been made by Olzewski[3] and Dewar,[4] that difficult task was accomplished in 1908 by Onnes.

Occurrence.—Helium, like many other "rare" elements, is widely distributed in nature, though in most cases it is found only in small quantities. It is present in the atmosphere and in sea- and river-water,[5] in the gases evolved from many mineral springs, and in most of the older rocks and minerals. It has been detected in at least one sample of meteoric iron; it exists, as already mentioned, in the sun; and spectroscopic observations lead to the conclusion that it is present in many other fixed stars and is indeed the chief constituent of the hottest of them.[6] The lines of helium are also seen in the spectra of many nebulæ and novæ.

The presence of helium in the atmosphere was detected spectroscopically first by Kayser at Bonn in August 1895[7] and, soon afterwards, by Friedlander at Berlin.[8] Ramsay, using Dewar's method of separation (*vide infra*), found that air contained 0·000056 per cent. by weight and 0·00040 per cent. by volume of helium; *i.e.* about 1 volume of helium in 250,000 volumes of air;[9] this, however, is obviously a minimum value, and Watson,[10] from an analysis of the gas separated from air by Claude's method (*vide* Neon, p. 325), concludes that the amount is more probably of the order of 1 volume in 185,000 volumes.

Helium has been detected in the gases evolved from many mineral springs. The following is a list of some of the more important:—

Five springs at Bois (Cauterets);[11] several springs at Wildbad (Black

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[1] Ramsay and Soddy, *Proc. Roy. Soc.*, 1903, **72**, 204; **73**, 346.

[2] Sir J. J. Thomson, *Rays of Positive Electricity* (Longmans & Co., 1913), p. 122; *cf.* Ramsay, *Nature*, 1912, **89**, 502.

[3] Olzewski, *Wied. Annalen*, 1896, [iii.], **59**, 184; *Bull. Acad. Sci. Cracow*, 1905, 407; *Ann. Chim. Phys.*, 1906, [viii.], **8**, 139.

[4] Dewar, *Trans. Chem. Soc.*, 1898, **73**, 533; *Compt. rend.*, 1904, **139**, 421. See also Travers, Senter, and Jaquerod, *Phil. Trans.*, 1903, A, **200**, 131.

[5] Troost and Ouvrard, *Compt. rend.*, 1895, **121**, 394.

[6] Lockyer, *Proc. Roy. Soc.*, 1898, **62**, 52.

[7] Kayser, *Chem. News*, 1895, **72**, 89.

[8] Friedlander, *Zeitsch. physikal. Chem.*, 1896, **19**, 657.

[9] Ramsay, *Proc. Roy. Soc.*, 1905, A, **76**, 111; 1908, A, **80**, 599.

[10] Watson, *Trans. Chem. Soc.*, 1910, **97**, 810.

[11] Ramsay and Travers, *Proc. Roy. Soc.*, 1896, **60**, 442; Bouchard, *Compt. rend.*, 1895, **121**, 392.

Forest);[1] Baillière (Pyrenees);[2] Bagnoles de l'Orne;[3] Monte Irone (Abano) and Casotto and Tini *soffioni* (Larderello, Tuscany); Mazières, Côte d'Or, and many other springs;[4] the Bath springs.[5]

The gases at Mazières contain 5·4 per cent. of helium, and might well serve as a source of the gas.

Cady and MacFarland[6] have made a minute examination of a large number of samples (47) of natural gas from different localities in Kansas, U.S.A., especially with reference to the amounts of helium contained in them. Some helium was found in all but two samples, and the proportion present, in general, increased with increasing amounts of nitrogen and decreased with increase in the amount of paraffins. It is possible to trace lines of approximately equal content of helium and paraffins, and it is found that these run across the State from N.E. to S.W., and show a general correspondence with the lines of outcrop of the various geological strata. In four of the samples the amount of helium was over 1 per cent. by volume:—

Dexter, Cowley County, ...	1·84 per cent.
Dexter, Greenwell Well, ...	1·64 ,,
Eureka, New Field, ...	1·50 ,,
Eureka, Town Supply, ...	1·50 ,,

It has been found that about 0·17 per cent. by volume of helium is contained in the inflammable gas which has for many years blown from a hole in the carnallite bed in the underground workings at Leopaldshall (Stassfurt).[7] Similarly, both helium and argon have been found in gas blown off from the rock-salt at Karlsbad.[8] Helium varying in amount from ·0141 per cent. to ·0011 per cent. occurs in the natural gases of Kissármás (Hungary), Pechelbronn, Wels (Austria), and Neuengamme (Hamburg): the gas from a deep well boring in Alsace contained 0·38 per cent. of helium.[9]

It has been calculated by Dr Johnstone Stoney[10] that a gas having the low density of helium could not be retained permanently by a planet of the earth's mass; it seems probable that the constancy of the proportion of helium in the atmosphere is due to a balance between two factors—the loss of helium into space and its continual emission from sources such as those mentioned. It has been calculated that nine of the mineral springs investigated give off in the aggregate about 12,000 litres of the gas annually.[11]

Helium is present, usually alone, but in some cases accompanied by argon, in a large number of minerals and rocks, and a considerable body of evidence has been accumulated which indicates that its presence is to be ascribed to the disintegration of radioactive material that is or has been contained in these substances. There is reason to believe that the helium in natural gas is mainly "fossil," and not of recent formation.[1]

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[1] Kayser, *Chem. News*, 1895, **72**, 89.

[2] Bouchard, *loc. cit.*

[3] Bouchard and Desgrez, *Compt. rend.*, 1896, **123**, 969.

[4] Moureu, *Compt. rend.*, 1895, **121**, 819; 1904, **139**, 852; 1906, **142**, 1155; Moureu and Biquard, *ibid.*, 1906, **143**, 795.

[5] Ramsay, *Proc. Roy. Soc.*, 1896, **60**, 56. See also Pesendorfer, *Chem. Zeit.*, 1905, **29**, 359; Prytz and Thorkelssohn, *Chem. Zentr.*, **1905**, [ii.], 1570; Ewers, *ibid.*, **1906**, [i.], 1319.

[6] Cady and M'Farland, *J. Amer. Chem. Soc.*, 1907, **29**, 1523.

[7] Erdmann, *Ber.*, 1910, **43**, 777.

[8] Pesendorfer, *Chem. Zeit.*, 1905, **29**, 359.

[9] Czakó, *Zeitsch. anorg. Chem.*, 1913, **82**, 249. For helium in coal mine gases, see Moureu and Lepape, *Compt. rend.*, 1914, **158**, 598.

[10] Stoney, *Chem. News*, 1895, **71**, 67.

[11] Moureu and Biquard, *Compt. rend.*, 1908, **146**, 435.

The most important helium minerals are: clèveite and other species of pitchblende, monazite, fergusonite, bröggerite, samarskite, thorianite, and euxenite.[2] Other minerals in which helium has been found are: Naegite, yttrotantalite, annerodite, thalenite, malacone, carnotite, beryl, torbernite, wohlerite, pyrochlore, polycrase, trogerite, xenotime, gummite, thorite-orangeite, niobite-columbite, sphene, rutile, and zircon; also in the Stassfurt minerals, sylvine, carnallite, kieserite, and rock-salt, in native bismuth (Saxony),[3] and in beryllium minerals.[4]

The existence of helium in a meteorite (from Augusta County, Virginia, U.S.A.) affords additional evidence in favour of the conclusion that the element is widely distributed throughout our solar system.[5]

Isolation.—The chief available sources of helium are the air, certain minerals, and a few mineral springs. Originally the cheapest way of preparing helium was, undoubtedly, by heating a suitable mineral, *e.g.* monazite sand or clèveite, either alone or with dilute sulphuric acid.

The apparatus used for the preparation of helium according to this method may be of the form depicted in fig. 79. The finely powdered mineral is placed in the iron tube T, which is heated to redness in a suitable furnace. The open end of this tube is fitted with a rubber stopper carrying a single delivery tube, and the small water-jacket W cools the end of the tube that projects from the furnace and protects the rubber connection from injury. The evolved gas is freed from water and carbon dioxide by passage over solid potash in the vessel D and is finally collected in a reservoir R filled with mercury or strong potash solution according as the amount of gas dealt with is small or large. The tube P connects with a Topler pump, and the open manometer M indicates the pressure within the apparatus.

In carrying out an experiment the mineral is introduced into the iron tube and the whole apparatus is evacuated. On heating the tube a slow evolution of gas commences and continues for many hours. When the pressure within the apparatus becomes equal to the atmospheric pressure the gas is collected in the reservoir R, until the evolution practically ceases. R is then shut off and the residual gas removed from the other part of the apparatus and transferred either to R or to another reservoir.

A modification of this method consists in heating the mineral in an atmosphere of carbon dioxide (prepared from magnesite by heating) and collecting the gas over potash.[6] It is stated that the best results are obtained by heating the mineral to 1000° - 1200° C. in a porcelain tube.[7]

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[1] Czakó, *loc. cit.*; Moureu and Lepape, *Compt. rend.*, 1912, 155, 197; 1911, 158, 839.

[2] Ramsay, *Proc. Roy. Soc.*, 1896, 59, 325; Ramsay and Travers, *ibid.*, 60, 442; Ramsay, Collie, and Travers, *Trans. Chem. Soc.*, 1895, 67, 689; Olzewski, *Bull. Acad. Sci. Cracow*, 1905, p. 407.

[3] Bordas, *Compt. rend.*, 1908, 146, 896; Waters, *Phil. Mag.*, 1909, [vi.], 18, 677, 19, 903; Thomsen, *Zeitsch. physikal. Chem.*, 1898, 25, 112; Benedicks, *Bull. Geol. Inst. Univ. Upsala*, 1899, 4, 1; Lange, *Zeitsch. Naturwiss.*, 1910, 82, 1; Tschernik, *J. Russ. Chem. Soc.*, 1897, 29, 291; Kitchin and Winterson, *Trans. Chem. Soc.*, 1906, 89, 1570; Strutt, *Proc. Roy. Soc.*, 1908, A 81, 278; Hogley, *Phil. Mag.*, 1909, [vi.], 18, 672; Piutti, *Le Radium*, 1910, 7, 116.

[4] Piutti, *Atti R. Accad. Lincei*, 1913, [v.], 22, i., 140.

[5] Ramsay, *Compt. rend.*, 1895, 120, 1049; for an analysis of this meteorite, see Mallet, *Amer. J. Sci.*, 1871, [iii.], 2, 10.

[6] Langlet, *Zeitsch. anorg. Chem.*, 1895, 10, 289.

[7] Sieverts and Bergner, *Ber.*, 1912, 45, 2576.

Another method which is more expeditious and gives a better yield is to heat the mineral with about its own weight of acid potassium sulphate in a hard glass tube. The mixture is very liable to froth, and the tube should not be more than half full.

Most minerals give the largest yield of helium when boiled with dilute sulphuric acid. This operation is best carried out in a round flask of hard glass, fitted as in fig. 80. The rubber stopper R fits some way into the conical neck so that a layer of mercury on the top makes all joints tight. The upper end of the condenser C can be connected at will either with a reservoir for the evolved gas or with a Töpler pump.

In performing an experiment the flask and the contained mineral (which must be finely powdered) are freed from air by introducing successive small quantities of water through the funnel F and pumping away the water-vapour. Dilute sulphuric acid (1 : 8), which has been boiled just previously to expel air, etc., is then run in and boiled with the mineral for about 30 minutes. When the gas evolved at atmospheric pressure has been collected, the reservoir is shut off and the residual gas removed from the rest of the apparatus through the pump and transferred to the reservoir.

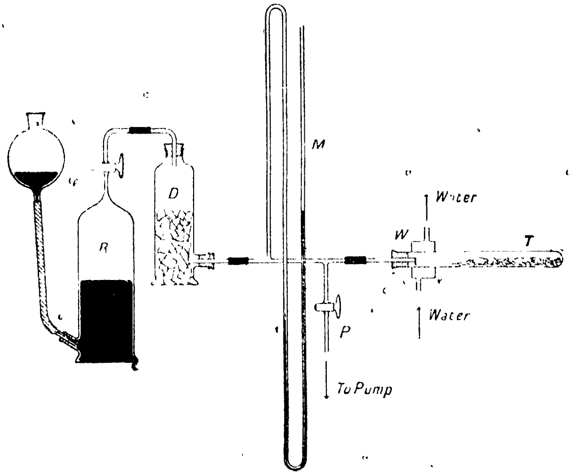

FIG. 79.

As 100 grams of clèveite will give over 500 c.c. of gas and can be obtained for about 10s., the cost of preparation of crude helium by this method works out at about £1 per litre. Other minerals available for the preparation of helium by this method (i.e. which yield from 1·0 to 1·5 c.c. or more of gas per gram) are fergusonite, samarskite, and monazite:[1] monazite sand was used by Onnes as the source of the large quantities of helium required for his researches upon its liquefaction.

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[1] Ramsay and Travers, *Proc. Roy. Soc.*, 1896, **60**, 442; 1897, **62**, 325.

Certain of the natural sources of helium mentioned above yield the gas in sufficient quantity to afford a useful supply of it. The chief of these are the springs of Bath and Mazières, the Tini *soffioni* at Larderello, and the natural gas wells of Dexter. The device illustrated in fig. 81 has been used by Ramsay in collecting the gas from mineral springs. The tin vessel V is provided with taps above and below (B, C), and both it and the tube A are first completely filled with water. On bringing the funnel attached to the tube A over the stream of gas rising through the water, and opening the taps B and C, the gas passes into V, while the displaced water flows back into the well. When gas is seen to issue from the lower end of C the vessel is known to be full, and the taps are closed.

An excellent method of obtaining helium, which would probably prove comparatively inexpensive where the necessary plant is available, is that devised by Claude. The apparatus used is described in detail under Neon (p. 325), and consists essentially of a modification of the column used for the isolation of pure oxygen and nitrogen by the fractionation of liquid air, whereby the most volatile gases are collected apart.

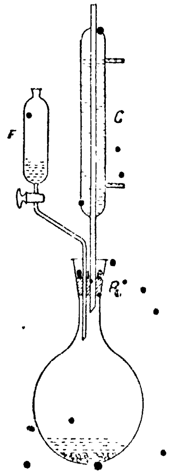

FIG. 80.

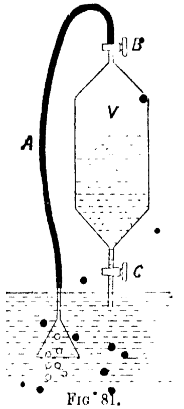

FIG. 81.

The fact that helium is a product of the radio-active disintegration of certain elements need only be mentioned here: the point will be dealt with more fully under Niton (p. 355), and under Radium, Vol. III. The identity of the helium atom with the α-particles given off during radio-active change may be regarded as well established, as Rutherford has shown that if any charged particles other than helium atoms are given off, their number does not exceed 1/10,000 of the number of helium atoms.[1]

Purification.—On account of its great volatility at very low temperatures, helium is more easily purified than any other member of the group. The usual procedure is to remove nitrogen and hydrogen, if present, by passing the crude helium over a heated mixture of quicklime and magnesium filings,[1] and then over red-hot copper oxide. In the case of gas from clèveite or monazite, which contains no appreciable amount of other inert gases, the résidue from this operation is already fairly pure helium. Should the gas contain argon, as, *e.g.*, when obtained from mineral springs, it is necessary to cool it to a low temperature by means of liquid air boiling under reduced pressure: any nitrogen or argon present is liquefied, and helium can be pumped off. Neon, if present, can be removed by cooling the gas with liquid hydrogen. At this temperature all gases are liquefied except helium.

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[1] Rutherford, *Phil. Mag.*, 1914, [vi.], 27, 488; *cf.* Nicholson, *ibid.*, 1911, [vi.], 22, 864.

The best method for the purification of helium, however, depends on the fact, discovered by Dewar,[2] that cocoanut charcoal at the temperature of liquid air completely absorbs all gases except helium. A suitable form of apparatus is indicated in fig. 82. The mixed gases are introduced into the apparatus from a gas-holder, allowed to remain in contact with the cold charcoal for half an hour, and the pure helium is finally removed through a Topler pump and collected in another gas-holder.

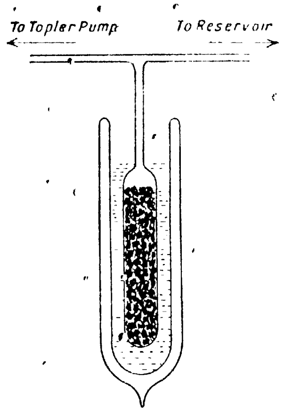

Fig. 82.

An investigation of the relative degrees of absorption of helium, neon, hydrogen, and nitrogen by cocoa-nut charcoal

Nitrogen at − 182°·5 C.		Hydrogen at − 195°·5 C.		Neon at − 195°·5 C.		Helium at − 195°·5 C.	
A.	B.	A.	B.	A.	B.	A.	B
935	0·004	10·5	0·0060	10·5	0·45	21	·27
1,870	0·010	21	0·0115	21	0·88	...	...
3,740	0·032	42	0·0205	32	1·30	...	...
4,660	0·083	84	0·0360	42	1·71	...	...
5,600	0·385	205	0·0830	84	3·50	...	...
6,530	1·107	371	0·176	122	5·30	...	...
8,400	8·75	840	0·475	163	7·20	...	...
9,300	11·50	1400	1·060	244	11·30	...	...
10,360	33·20	2800	3·50	325	15·50	...	...
11,200	90·0	4200	8·70	406	19·40	...	...
12,100	247·0	5600	20·60	618	30·50	...	...
...		6300	43·70	801	40·50	...	...

---

[1] Maquenne's method, see p. 331.

[2] Dewar, *Proc. Roy. Soc.*, 1904, 74, 122 and 127.

at low temperatures has been made by Claude.[1] The results are given in the preceding table, where the columns A give the volume in c.c. of gas absorbed by 100 gm. of charcoal, while the columns B give the corresponding gas pressure in mm. of mercury.

Leduc states that the absorption of helium in charcoal follows Henry's law, and in this respect, therefore, it differs from other gases.[2]

From a consideration of Claude's figures it will be evident that while the method can give a sharp separation of helium from hydrogen and nitrogen and is, consequently, excellent for the purification of helium from minerals, it can only separate helium and neon if used as a method of fractionation.

Small amounts of helium in a vacuum tube may be purified by taking advantage of the fact that the finely divided platinum deposited upon the walls of the tube by the prolonged passage of a discharge can absorb helium in considerable amount.[3] Nitrogen, argon, etc., remain unabsorbed, and may be pumped out of the tube, while the helium can then be driven out of the platinum deposit by heating the tube with a free flame.[4]

Jaquerod and Perrot[5] noticed that at a temperature of 1100° C. fused quartz is permeable to helium and hydrogen, but not to other gases, and upon this fact they based a method for the purification of helium.[6] Fig. 83 is a diagram of their apparatus. The quartz bulb B is enclosed within a wide platinum tube A into which the impure helium, mixed with 5 per cent. of oxygen, is introduced at a pressure slightly over 1 atmosphere. The interior of the bulb having been evacuated, the central part of the platinum tube is heated to the proper temperature, and the helium which diffuses into the bulb is pumped away into a reservoir.[7] The method is slow, but is stated to give a very pure product. Apparently the success of the experiment depends on the selection of a suitable sample of quartz for the bulb, as Watson attempted to use the method for the purification of helium, but found that the quartz of his apparatus would not allow the passage of more than traces of helium at the temperatures employed.

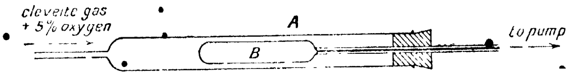

FIG. 83.—Apparatus for the purification of helium.

Properties.—Helium is a colourless gas, and possesses neither taste nor odour.[8]

The density of helium has been determined by many investigators; the more important results are tabulated below[8]:—

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[1] Claude, *Compt. rend.*, 1914, 158, 861.
[2] Leduc, *Compt. rend.*, 1914, 158, 864.
[3] Troost and Ouvrard, *Compt. rend.*, 1895, 121, 3[illegible].
[4] Travers, *Proc. Roy. Soc.*, 1897, 60, 449.
[5] Jaquerod and Perrot, *Compt. rend.*, 1904, 139, 789; *Arch. sci. phys nat.*, 1904, [iv.], 18, 613.
[6] But *cf.* under Neon, p. 326.
[7] Jaquerod and Perrot, *Compt. rend.*, 1907, 144, 135; see also Sieverts and Bergner, *Ber.*, 1912, 45, 2576.
[8] See Ramsay and Travers, *Proc. Roy. Soc.*, 1898, 62, 316.

Density (Oxygen = 16).	*Weight of Normal Litre.*	*Density* (Oxygen = 16).	*Weight of Normal Litre.*
2·01[1]	0·1795 gram	1·99[6]	0·1775 gram.
1·979[2]	0·177 ,,	2·04[6]	0·182 ,,
1·98[3]	0·177 ,,	2·02[6]	0·180 ,,
1·985[4]	0·1773 ,,	2·01[6]	0·179 ,,
2·00[5]	0·1785 ,,	1·995[7]	0·1782 ,,
		1·999[8]	0·17856 ,,

These figures agree very well, and it is probable that the last two results are very close approximations to the true value.

A study of the relation between the pressure and volume of the gas has shown that at 0° with pressures varying from 147 mm. to 838 mm. of mercury the product *pv* is absolutely constant, *i.e* the compressibility coefficient is zero.[9] Jaquerod and Scheuer give the compressibility coefficient at 0° as −0·00060 between pressures of 400 and 800 mm. of mercury.[10]

In this respect, therefore, helium behaves as it might be expected to do were its critical temperature much higher than it actually is. It may be noted in this connection that when helium and hydrogen are mixed the volume of the mixture is greater than the sum of the original volumes. The *pv* isothermals for helium have been determined over wide ranges of temperature and pressure by Onnes.[11]

The molecular weight of helium, calculated from Heuse's value for the density according to Berthelot's method of limiting densities (see this Vol., Part I., p. 133), is **4·00**.

As an example of the extreme lightness of helium it has been observed that by passing a stream of pure carbon dioxide through a porous tube sufficient helium diffuses in from the atmosphere to be detected spectroscopically after absorption of the carbon dioxide by caustic potash.[12]

The coefficient of increase of pressure at constant volume is perfectly normal,[13] and at temperatures from 0° to 100° C. has the value 0·0036616. This value is independent of the original pressure.[14]

It was early discovered that helium does not obey Graham's Law of diffusion of gases, but passes through a porous diaphragm more slowly than is expressed by the law.[1] Donnan observed later that the rate of effusion of helium through a small hole in a platinum plate was slower than one would expect from calculations based on the density, and suggested that the anomaly is probably due to the fact that at ordinary temperatures helium, like hydrogen, undergoes a rise in temperature on free expansion through a small orifice[2] (Joule-Thomson effect). All other known gases, with the exception of hydrogen, diffuse more rapidly than is required by calculations based on the assumptions of the kinetic gas theory.

---

[1] Langlet, *Compt. rend.*, 1895, **120**, 1212. *Note*—It seems improbable that the methods used by Langlet for the separation of helium from the crude clèveite gas could have given him a pure product, and the accuracy of his figure is most likely due to a balancing of errors.

[2] Ramsay and Travers, *Proc. Roy. Soc.*, 1898, **62**, 316.

[3] Ramsay and Travers, *Phil. Trans.*, 1901, **197**, 47.

[4] Schierloh, *cf.* reference (2).

[5] Olzewski, *Ann. Physik*, 1905, [iv.], **17**, 997.

[6] Onnes, *Comm. Phys. Lab. Leyden*, 1908, No. **108**.

[7] Watson, *Trans. Chem. Soc.*, 1910, **97**, 810.

[8] Heuse, *Ber. deut. physikal. Ges.*, 1913, **15**, 518.

[9] Burt, *Trans. Faraday Soc.*, 1910, **6**, 19.

[10] Jaquerod and Scheuer, *Mem. Soc. phys. nat.*, 1908, **35**.

[11] Onnes, *Proc. K. Akad. Wetensch. Amsterdam*, 1907, **10**, 445, 741; *Comm. Phys. Lab. Leyden*, 1907, No. 102. Holborn and Schultze *Ann. Physik*, 1915, [iv.], **47**, 1089.

[12] Rayleigh, *Phil. Mag.*, 1901, [vi.], **1**, 100.

[13] Kuenen and Randall, *Proc. Roy. Soc.*, 1895, **59**, 60.

[14] Onnes, *Proc. K. Akad. Wetensch. Amsterdam*, 1907, **10**, 589; Travers, Senter, and Jaquerod, *Proc. Roy. Soc.*, 1902, **70**, 484.

The *solubility* of helium in water was first determined by Estreicher,[3] who found the following values for the absorption coefficient: 0·01487 at 0·5°, and 0·01404 at 50°, with a minimum at 25°. The experimental procedure adopted, however, has since been shown to be untrustworthy.[4] More importance must be attached to the values obtained by Antropoff,[5] who found for the absorption coefficient the value 0·0131 at 0°, and 0·0226 at 50°, with a minimum at 10°. The existence of a minimum has its counterpart in the case of other inert gases (*q.v.*) and of hydrogen. Helium is insoluble in absolute alcohol and benzene.[6]

The *viscosity* of helium was first determined by Rayleigh by measurement of the rate of flow of the gas through a capillary tube. He obtained the value 0·96 (air = 1). Later, Schultze repeated this determination, and found the viscosity of helium at 15° to be 1·086 times that of air.[7]

Rankine has recently redetermined this constant, using an apparatus which may be described here, as it is particularly well adapted for use with very small amounts of gas, and therefore finds application in investigations on the rare gases. It consists of a tube in the form of an elongated O, one side of which, A (fig. 84), is a very fine capillary tube, while the other side, B, though much wider, is sufficiently narrow to allow a pellet of mercury, C, to remain intact. The driving pressure required to force the gas through the capillary is supplied by the weight of this pellet of mercury. Taps D and E allow the apparatus to be cleaned, evacuated, and filled with the gas under examination.[8]

The results obtained with this apparatus confirmed Schultze's figure.[9] Therefore, taking the absolute value for the viscosity of air at 15°·5 as $\eta = 1{\cdot}803 \times 10^{-4}$ C.G.S. units,[10] it follows that the absolute value of the viscosity of helium at 15° is $1{\cdot}958 \times 10^{-4}$ C.G.S. units, which is in fair agreement with the figure $1{\cdot}969 \times 10^{-4}$ at 15°·3 found experimentally by Tanzler.[11]

Tanzler also found $\eta = 2{\cdot}348 \times 10^{-4}$ at 99°·6 and $\eta = 2{\cdot}699 \times 10^{-4}$ at 184°·6. Assuming[12] that the change of viscosity follows a linear law of the type

$$\eta_\theta = \eta_0(1 + \beta\theta),$$

---

[1] Ramsay and Collie, *Proc. Roy. Soc.*, 1896, **60**, 206; confirmed by Hagenbach, *Wied. Annalen*, 1897, [iii.], **60**, 124.

[2] Donnan, *Phil. Mag.*, 1900, [v.], **49**, 423.

[3] Estreicher, *Zeitsch. physikal. Chem.*, 1899, **31**, 176.

[4] Fox, *Trans. Faraday Soc.*, 1909, **5**, 68.

[5] Antropoff, *Proc. Roy. Soc.*, 1910, **A**, **83**, 474.

[6] Ramsay, *Ann. Chim. Phys.*, 1898, [vii.], **13**, 462.

[7] Schultze, *Ann. Physik*, 1901, [iv.], **6**, 302.

[8] Rankine, *Proc. Roy. Soc.*, 1910, **A**, **83**, 265.

[9] Rankine, *ibid.*, p. 516.

[10] Rankine, *ibid.*, p. [illegible]

[11] Tanzler, *Ber. deut. physikal. Ges.*, 1906, **4**, 222. *See also* Vogel, *Ann. Physik*, 1914, [iv.], **43**, 1235; Onnes and Weber, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1396, 1899. Gille, *Ann. Physik*, 1915, [iv.], **48**, 799.

[12] Rankine, *Proc. Roy. Soc.*, 1910, **A**, **84**, 181.

where η_θ and η_0 are the values of the viscosity at $\theta°$ and $0°$ respectively, the value of the temperature coefficient β for helium is $2·32 \times 10^{-3}$.

The *thermal conductivity* of a gas, according to the kinetic gas theory, is given by K in the equation

$$K = f.\eta.c_v,$$

where η and c_v are the viscosity and the specific heat at constant volume respectively, and f is a constant. For helium the value of K at 0° C. is 0·00003386,[1] from which it follows that $f = 2·507$ – a value which is in accordance with Boltzmann's development of Maxwell's theory, and therefore affords evidence of the molecular simplicity of the gas.[2] The thermal conductivity at low pressures shows unexplained anomalies.[3]

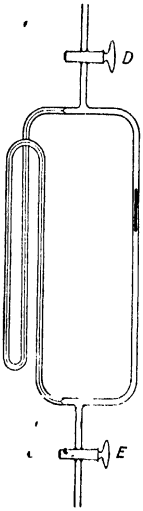

FIG. 84.

The *refractivity* of helium was first determined by Rayleigh.[4]

The method used consisted in passing parallel beams of light from the same source through similar tubes containing helium and air respectively. The pressure of gas in these tubes was varied until a point was reached at which the retardation of light, as determined by observation of interference bands, was the same in both tubes. The ratio of the refractivities is then inversely as the ratio of the pressures in the tubes and, the refractivity of air being known, that of helium may readily be calculated.

Rayleigh's figure was inaccurate, but Ramsay and Travers subsequently repeated the measurements, and found the refractivity of helium ($\mu - 1$) to be 0·1238 times that of air. This gives for helium the value[1]

---

[1] Schwarze, *Ann. Physik*, 1903, [iv.], **11**, 303.

[2] See also Wachsmuth, *Physikal. Zeitsch.*, 1908, **9**, 235; and Winkler, *Zeitsch. physikal. Chem.*, 1906, **55**, 344.

[3] Soddy and Berry, *Proc. Roy. Soc.*, 1911, A, **85**, 81.

[4] Rayleigh, *Proc. Roy. Soc.*, 1896, **59**, 205.

$$\mu = 1·0000361.$$

The above method or some modification of it has been used by other observers, the chief of whose results are tabulated below.

	Wave Length.	*Refractive Index* (μ).
(1)[2]	Visible spectrum (14°) . . .	1·0000340
(2)[3]	6438	1·000034060
	5790, 5760, (N.T.P.) . . .	1·000034384
	5461 ,,	1·000034525
	4359 ,, . . .	1·000035335
(3)[4]	(D_1) ,, ...	1·00003500

It has been the custom to express the refractive index of a gas by an equation of the type—

$$\mu - 1 = a\left(1 + \frac{b}{\lambda^2}\right) \quad . \quad . \quad . \quad . \quad (i.)$$

which may be written:

$$\mu = A + \frac{B}{\lambda^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii.)$$

The values of the constants in these equations for helium are as follows:—

	a.	b.	A.	B.
(4)[5]	·00003478	$2·2 \times 10^{-11}$	1·00003478	$7·5 \times 10^{-16}$
(5)[6]	·0000347	$2·4 \times 10^{-11}$	.	...

C. and M. Cuthbertson prefer to employ an equation of the Sellmeier type:—

$$\mu - 1 = \frac{C}{\eta_0^2 - \eta^2},$$

where η_0 is the frequency of the free vibration and η is the frequency of the light for which μ is to be calculated.[7]

For helium at N.T.P. the constants in this equation are[8]:—

$$C = 2·42476 \times 10^{27}: \eta_0^2 = 34991·7 \times 10^{27}.$$

The *dispersion* of helium is extremely small, as may be seen by the smallness of the constant b in equation (i.) above, as compared with its value in the case of hydrogen or argon ($b = 4·3 \times 10^{-11}$ for hydrogen, and $b = 5·6 \times 10^{-11}$ for argon). This is perhaps clearer if we express relative dispersion by the formula—

$$\frac{1}{\nu} = \frac{\mu_F - \mu_C}{\mu_D - 1},$$

---

[1] Ramsay and Travers, *Proc. Roy. Soc.*, 1901, 67, 331.

[2] Scheel and Schmidt, *Ber. deut. physikal. Ges.*, 1908, 6, 207; method given, *ibid.*, 1907, 5, 24.

[3] Hermann, *ibid.*, 1908, 6, 211.

[4] Burton, *Proc. Roy. Soc.*, 1908, A, 80, 390.

[5] Burton, *loc. cit.*

[6] C. Cuthbertson and Metcalfe, *Proc. Roy. Soc.*, 1908, A, 80, 411.

[7] C. and M. Cuthbertson, *Proc. Roy. Soc.*, 1910, A, 83, 154.

[8] C. and M. Cuthbertson, *ibid.*, 1910, A, 84, 15.

where μ_F, μ_C, μ_D are the refractive indices for the Fraunhofer lines F, C, and D. We then have the following values of v:—

Air = 98·0
Hydrogen = 65·9
Helium = 39·9

The *specific inductive capacity* of helium has been determined by the electrostatic null-method of Hopkinson and Lebedeff, and has the value

$$K = 1{\cdot}000074$$

at 0° and 760 mm.[1] According to Maxwell's Law, K should be equal to $(\mu_\infty)^2$, where μ_∞ is the refractive index for radiations of large wave-length. Extrapolating from the values for the refractive index for light of various wave-lengths within the range of the visible spectrum, we find $\mu_\infty = 1{\cdot}0000375$,

whence $$(\mu_\infty)^2 = 1{\cdot}000075,$$

a value which agrees well with that given above for K.[2] Bouty states that the *dielectric cohesion*[3] of helium at 17° is represented by the number 18·3 (A = 38; air = 419; $H_2 = 205$).[4] In this connection the extraordinary length of the spark gap in helium may be mentioned. By experiments made with a vacuum tube of which one electrode was movable, it was found that under a certain fixed set of conditions as to potential difference, pressure, etc., the following lengths of spark were obtainable in helium, and in certain other gases:—

Oxygen	23·0 mm.
Air	33·0 „
Hydrogen	39·0 „
Argon	45·5 „
Helium	250–300 mm.[5]

If V_{He} and V_{air} are the sparking potentials in helium and air respectively, then the ratio V_{He}/V_{air} is found to diminish with increase of sparking distance (δ) and with increase of pressure (P), while other gases compared with air show an increase of sparking potential with increase in δ and P. When V is plotted against δ, helium gives straight lines, while other gases give curves concave to the axis of δ.[6] The minimum spark potential in helium is 184 volts, and the corresponding pressure is 2·4 mm.[7]

The *spectrum* of helium is complex, and was found by Runge and Paschen to contain six series of lines. These fall naturally into two groups in each

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[1] Hochheim, *Ber. deut. physikal. Ges.*, 1908, **6**, 446.

[2] Dobroserdoff, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1164.

[3] When a gas, at pressure p cms. of mercury, is enclosed in a suitable insulating vessel and exposed to the influence of a gradually increasing electrostatic field of force, it is found that when the strength of the field reaches a certain value, y volts per cm. say, the gas suddenly becomes a conductor of electricity. At constant temperature it is found that if the thickness of the gas layer and the value of p are not too small,

$$y = a + bp,$$

where a and b are constants. The coefficient b is called the *dielectric cohesion* of the gas, and is inversely proportional to the absolute temperature.

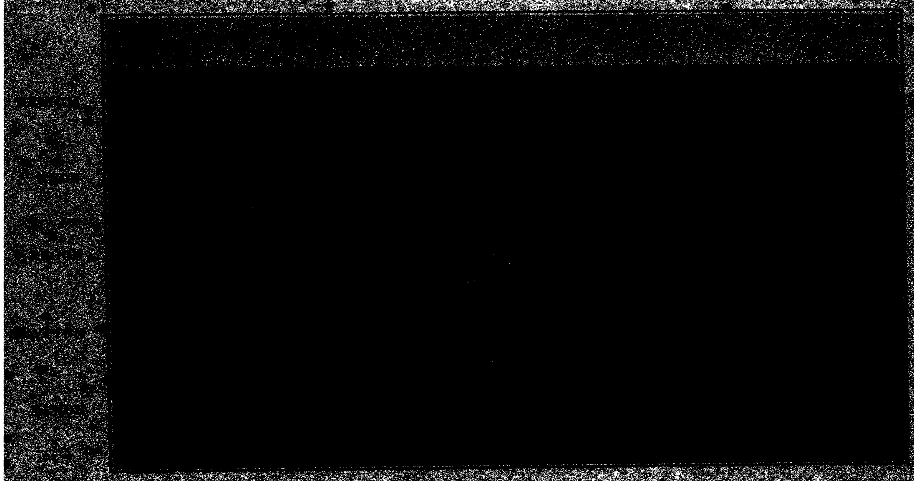
[4] Bouty, *Compt. rend.*, 1907, **145**, 225; *Ann. Chim. Phys.*, 1911, [viii.], **23**, 5; 1913, [viii.], **28**, 545.

[5] Collie and Ramsay, *Proc. Roy. Soc.*, 1895, **59**, 257; *cf.* Natterer, *Wied. Annalen*, 1889, p. 663.

[6] Ritter, *Ann. Physik*, 1904, [iv.], **14**, 118.

[7] Watson, *Proc. Camb. Phil. Soc.*, 1913, **17**, 90.

SPECTRA OF THE INERT GASES.



Spectra produced in Ordinary Vacuum Tubes by the Uncondensed Discharge from an Induction Coil.

of which we have a Principal Series and two Subordinate Series which converge toward a common limit.[1]

One of these groups consists of doublet series, and the doublet D_3, by which helium was discovered, is the first in the Principal Series. It is the lines of this group which characterise the solar spectrum of helium, and the spectrum obtained in a vacuum tube under moderately low pressures.

The chief line of the Principal Single Line Series is λ5016, in the green, and is prominent in the spectrum of helium under very low pressure.[2] Generally all the lines of helium are visible in the spectrum under any conditions; but the relative intensity of the two groups characterised by D_3 and λ5016 respectively can undergo great changes, so that the light emitted by a vacuum tube exhibits the following alterations as the pressure is reduced[3]:—

1. Orange yellow.
2. Bright yellow.
3. Yellowish green.
4. Green.
5. Green X-ray vacuum.
6. Black vacuum.

Lists of the series lines of the spectrum are given below[4]:—

FIRST GROUP.

Principal Series.	*Diffuse Series.*	*Sharp Series.*	*Principal Series.*	*Diffuse Series.*	*Sharp Series.*
λ = 3888·97	λ = 5876·21	λ = 7065·77	λ = 2723·3	λ = 3634·52	λ = 3652·29
3888·76	5875·88	7065·51	2696·5	3434·39	3652·15
3187·98	4471·85	4713·39	2677·1	3587·54	3599·59
3187·83	4471 66	4713 17		3587·42	3599·45
2945·35	4026·52	4121·15		3554·5	3563·26
2945·22	4026·25	4120·98		3530·6	3563·11
2829·32	3819·89	3867·77		3512·6	3536·9
2829·16	3819·75	3867 61		3498·7	3517·5
2764·01	3705·29	3733·15		3487·8	3502·5
2763·91	3705·15	3733·01		3479·2	3490·8
					3481·5

SECOND GROUP.

Principal Series.	*Diffuse Series*	*Sharp Series.*	*Principal Series.*	*Diffuse Series.*	*Sharp Series.*
λ = 5015 73	λ = 6678·1	λ = 7281·8	λ = 3354 7	...	λ = 3878·3
3965·08	4922·08	5047·82	3296 9		3838·2
3964·84	4388·11	4437·73	3258·3		3808·3
3613·89	4143·91	4169·12	3231·3		
3613·78		4024·14	3213·4		
3447·72		3936·1			

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[1] Ritter, *Ann. Physik*, 1904, [iv.], 14, 118.

[2] Runge and Paschen, *Phil. Mag.*, 1895, [v.], 40, 297.

[3] Travers, *Proc. Roy. Soc.*, 1897, 60, 449.

[4] See Runge and Paschen, *loc. cit.*; Crookes, *Chem. News*, 1895, 72, 87; Vogel, *Sitzungsber. K. Akad. Wiss. Berlin*, 1895, p. 947; Eversheim, *Zeitsch. wiss. Photochem.*, 1910, 8, 148; Collie, *Proc. Roy. Soc.*, 1902, 71, 25. For a band spectrum associated with helium, see Goldstein, *Ber. deut. physikal. Ges.*, 1913, 15, 402; Curtis, *Proc. Roy. Soc.*, 1913, A, 89, 146. Fowler, *ibid.*, 1915, A, 91, 208. Nicholson, *ibid.*, p. 432.

The infra-red spectrum of helium has been investigated by Paschen.[1]

A series of lines observed by Pickering in the spectrum of the star ζ Puppis, and ascribed for many years to hydrogen, has been shown to belong to the spectrum of helium by Fowler, who has also observed new lines in this series; and Fowler has observed still another series in the helium spectrum, beginning with the well-known solar line λ 4686

Collie[3] observed that in the presence of mercury a Plucker tube containing helium showed the full spectrum in the capillary portion, but in other parts of the tube gave a spectrum modified in a way which corresponded to the change produced by change of pressure He suggests that a helium mercury tube containing a trace of hydrogen would form a useful spectroscopic standard as it gives a number of brilliant lines fairly evenly spaced throughout the visible spectrum.[4]

The *Doppler effect* is the change in wave-length of light wave due to relative motion in the line of sight of the light source and the observer. If a source of light is approaching an observer with velocity v, the change in wave-length ($d\lambda$) is given by

$$d\lambda/\lambda = v/c$$

where c is the velocity of light, the wave-length being diminished; and *vice versa* for a receding source. Until 1905, observations of this effect were limited to astronomical work on spectra, but in that year Stark discovered that the Doppler effect could be observed with the spectra of the "positive rays" or "Kanalstrahlen" of gases.[5] The discovery is an important one, as it promises to throw considerable light upon the question of the origin of series in spectra.[6] The *Doppler effect* has been observed for certain lines in the spectrum of helium [7]

The light of a vacuum tube containing helium is easily affected by electrical waves, and this fact forms the basis of a suggested method for their detection [8]

The *Zeeman effect* for helium has been observed by Lohmann.[9] When the glowing gas is placed in a magnetic field and the light issuing at right angles to the lines of force examined with an echelon diffraction grating, it is found that all the lines become triplets and that the fraction x/λ^2, where x is the distance between the outside lines of a triplet and λ is the mean wave-length, is the same for all lines. Measurements made with a Rowland grating give similar results [10] The simplest development of Lorentz's theory of the Zeeman effect leads to the anticipation that x/λ^2 should be the same for all the lines of a spectrum and the above experimental results therefore indicate that the helium molecule has a very simple structure. This conclusion receives support from the fact that mercury vapour, which is known on quite other grounds to be monatomic, shows precisely the same relationship.[1]

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[1] Paschen, *Ann. Physik*, 1910, [iv.], **33**, 717.

[2] Pickering, *Astrophys. J.*, 1896, **4**, 369; 1897, **5**, 92; Fowler, *Monthly Notices, R. Astronom. Soc.*, 1912, **73**, 62, *Nature*, 1913, 23rd October, p. 232; *Phil. Trans.*, **1914**, **A**, **214**; Bohr, *Phil. Mag.*, 1913, [vi.], **26**, 1, 476, 857; 1914, [vi.], **27**, 506, 1915, [vi.], **30**, 394. Evans, *ibid.*, 1915, [vi.], **29**, 281 Stark, *Ber. deut. physikal. Ges.*, 1914, **16**, 468. Stark and Wendt, *Ann. Physik*, 1914, [iv.], **43**, 983.

[3] Collie, *loc. cit.*

[4] See also Eversheim, *loc. cit.*

[5] Stark, *Physikal. Zeitsch.*, 1905, **6**, 892; *Ann. Physik*, 1906, [iv.], **21**, 451; Stark, Fischer, and Kirschbaum, *ibid.*, 1913, [iv.], **40**, 499; **42**, 241.

[6] For summary, see Sir J. J. Thomson, *Rays of Positive Electricity* (Longmans & Co., 1913); for references to 1913, see Fulcher, *Jahrb. Radioaktiv. Elektronik.*, 1913, **10**, 82.

[7] For details, see Dorn, *Physikal. Zeitsch.*, 1907, **8**, 589; Stark, Fischer, and Kirschbaum, *loc. cit.* Koch, *Ann. Physik*, 1905, [iv.], **48**, 98.

[8] Dorn, *Ann. Physik*, 1905, [iv.], **16**, 784.

[9] Lohmann, *Zeitsch. Wiss. Photochem.*, 1908, **6**, 1 and 41; *Physikal. Zeitsch.*, 1908, **9**, 145.

[10] Purvis, *Proc. Camb. Phil. Soc.*, 1909, **15**, 45.

Helium is diamagnetic.[2]

Experiments on the *absorption of cathode rays* in helium and in other gases have shown that with all gases the absorption increases to a maximum with decreasing velocity of the rays. In the case of hydrogen this maximum occurs with much lower velocities and is attained more suddenly than in the case of other gases, and helium exhibits the peculiar behaviour of hydrogen, but in a much exaggerated form: the absorption curve rises but slowly down to very small velocities of the rays and then rises very abruptly to a maximum.[3]

Numerous experiments have been made to find the *ratio of the two specific heats* (at constant pressure and constant volume). This determination is important, because from theoretical considerations and from measurements on the monatomic vapour of mercury, we believe that in any monatomic gas the value of the ratio C_p/C_v should be 1·667.[4]

One of the most convenient methods for determining this quantity depends on the relation between the ratio of the specific heats (γ) and the velocity of sound in the gas.

The velocity v of the propagation of sound waves in an elastic medium, according to Newton's formula, is:

$$v = \sqrt{\frac{K}{d}},$$

where K is the coefficient of elasticity and d the density of the medium. The value of K for a gas is the elasticity under adiabatic compression (without loss or gain of heat), and is greater than the isothermal elasticity, which is numerically equal to the pressure. The ratio between the two elasticities is equal to γ, the ratio of the specific heats.

If, therefore, in the gas under investigation, λ is the wave length of a sound of frequency n, and if the isothermal elasticity is p and its density d, we have

$$n\lambda = \sqrt{\frac{p\gamma}{d}} = \sqrt{\frac{\gamma}{D}},$$

where D is the density of the gas under unit pressure. Writing λ_1 and D_1 for the corresponding quantities in another gas for which the value of γ_1 is known, the wave-length λ_1 of a note of the same frequency n, will be given by

$$n\lambda_1 = \sqrt{\frac{\gamma_1}{D_1}}, \qquad \text{whence} \qquad \frac{\gamma}{\gamma_1} = \frac{\lambda^2 D}{\lambda_1^2 D_1}.$$

As the ratio p/d is independent of the pressure, we do not require to know the actual pressures and densities of the gases in the two cases, and any variation of temperature can be allowed for in the values of D and D′, though it is usual, for the sake of simplicity, to adopt the same temperature in each case.

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[1] Gray and Stewart, *Proc. Roy. Soc.*, 1903, 72, 16; *cf.* Voigt, *Nachr. K. Ges. Wiss. Gottingen*, 1911, p. 71.

[2] Tänzler, *Ann. Physik*, 1907, [iv], 24, 931.

[3] Robinson, *Physikal. Zeitsch.*, 1910, 11, 11.

[4] See this Vol., Part I., p. 97.

Air, for which $\gamma = 1·408$, is used as the standard gas, and the determination of γ for any other gas thus resolves itself into a comparison of the wave-lengths of the same sound in air and in the gas. This is usually accomplished by a method due to Kundt

The particular form of apparatus used by Ramsay, Collie, and Travers (*vide infra*) is indicated in fig. 85.

A long tube T, which may be of narrow bore (2 mm.) is closed at one end, and through this end is sealed a glass rod R, half of which is inside and half outside the tube. Some lycopodium powder is distributed along the tube, dry air is introduced, and the rod R is set into longitudinal vibration by rubbing it with a rag wet with alcohol. By moving the clip C on the thick-walled rubber tubing fitted to the open end of T, the length can be adjusted till it resounds to the note. The stationary waves thus set up in the tube by interference between the waves incident upon and reflected from the ends of the tube are made evident by the disposition of the lycopodium which is swept away from the points of greatest movement and heaped up at the nodes. The distance between adjacent nodes—the half wave-length—is determined by direct measurement. The tube is next evacuated and filled with the gas under examination and the measurement of wave-length repeated.

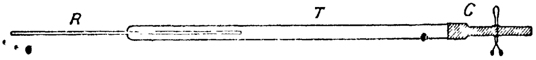

FIG. 85.

Owing to the lightness of helium it is extremely difficult to get good dust figures, and thus Ramsay at first found for γ the high value 1·8.[1] Subsequently it was found that in the particular apparatus used,

for air, $\lambda/2 = 19·60$ mm.
while for helium $\lambda/2 = 101·5$ „
Whence, for helium, $\gamma = 1·652$ „

This figure has been confirmed by other observers.[2]

Scheel and Heuse have determined the specific heat of helium at constant pressure and the ratio of the specific heats at 18° and −180°, with the following results:—

C_p at 18° . . 4·993 ; at −180° . . 4·934
γ at 18° . . 1·660 ; at −180° . . 1·673

while Eggert[4] found C_p to be practically independent of the temperature between −15° and 150° C. and equal to 5·065.

Liquefaction of Helium.—The failure of many attempts to liquefy helium suggested that its critical temperature must be very low, and from the behaviour of the gas in a vacuum tube connected with a charcoal absorption tube Dewar concluded that its boiling-point was not higher than 6° absolute.[2]

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[1] Ramsay, *Proc. Roy. Soc.*, 1895, **58**, 81.

[2] $\gamma = 1·652$, Ramsay, Collie, and Travers, *Trans. Chem. Soc.*, 1895, **67**, 696 ; $\gamma = 1·63$, Behn and Geiger, *Ber. deut. physikal. Ges.*, 1907, **5**, 657 ; $\gamma = 1·67$, Langlet, *Zeitsch. anorg. Chem.*, 1895, **10**, 289.

[3] Scheel and Heuse, *Sitzungsber. K. Akad. Wiss. Berlin*, 1913, p. **44**.

[4] Eggert, *Ann. Physik*, 1914, [iv.], **44**, 643.

The actual liquefaction of helium was preceded by a study of the isothermals down to the temperature of liquid hydrogen,[3] from which it appeared probable that at low temperatures the value of K for the Joule-Thomson effect (*cf.* p. 32) would change sign, and that at the temperature of solid hydrogen the expansion of helium from a considerable pressure would cause a lowering of temperature sufficient to make a self intensive cooling process successful. That this would be so had been predicted by Dewar[4]

Onnes prepared his helium from monazite sand and purified it by Dewar's method of fractionation from cold charcoal. The gas was circulated through an apparatus in which it was cooled first to the temperature of liquid air, then to 15° absolute by means of liquid hydrogen boiling under 60 mm. pressure, and finally passed through a specially constructed liquefier of the Hampson type. Thus 60 c.c. of liquid was obtained in 3 hours from 300 litres of gas.[5]

Liquid helium is a colourless, very mobile liquid. Its density is 0·154, and it is thus much lighter than any other known solid or liquid; it is stated to have a point of maximum density at about 2° absolute.[6] The ratio of the densities of liquid helium and its vapour at the boiling-point is 11 : 1. Calculating from the density by the formula of Lorentz and Lorenz, the refractive index is found to be 1·03.[7] By an ingenious device it was made possible to have a clear view of the liquid that collected in the vacuum-jacketed tube of the liquefier, and it was observed that the meniscus was sharply visible and straight: this indicates that the surface tension is very small. The boiling-point is about 4·3° absolute, the critical temperature is 5·25° absolute,[8] and the critical pressure is 2·26 atmospheres. The calculated critical volume is ·00271.

The following table shows the vapour pressure of liquid helium at temperatures below its critical temperature[8]:—

Absolute temperature .	4·28	4·97	5·10	5·15	5·22	5·25
Vapour pressure, mm. .	767	1329	1520	1569	1668	1718

Solid helium has not yet been obtained: efforts to produce it by evaporation of the liquid under reduced pressure have failed, although a temperature in the neighbourhood of 2·5° absolute has been reached.[9] It seems probable that the triple-point pressure of helium is below 10 mm. of mercury.

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[1] See, *e.g.*, Olzewski, *Wied. Annalen*, 1896, [iii.], **59**, 184; *Bull. Acad. Sci. Cracow*, 1905, p. 407; *Ann. Physik*, 1905, [iv.], **17**, 994; *Ann. Chim. Phys.*, 1906, [viii.], **8**, 139; Dewar, *Trans. Chem. Soc.*, 1898, **63**, 533; Onnes, *Proc. K. Akad. Wetensch. Amsterdam*, 1908, **10**, 744; Travers, Senter, and Jaquerod, *Phil. Trans.*, 1903, **A**, **200**, 131.

[2] Dewar, *Compt. rend.*, 1904, **139**, 421.

[3] Onnes, *Comm. Phys. Lab. Leyden*, 1907, No. **102**.

[4] Dewar, *Proc. Roy. Soc.*, 1901, **68**, 360. *Cf.* Onnes, *Nature*, 1908, **77**, 581.

[5] Onnes, *Proc. K. Akad. Wetensch. Amsterdam*, 1908, **11**, 168; *Compt. rend.*, 1908, **147**, 421.

[6] Onnes, *Comm. Phys. Lab. Leyden*, No. **119**.

[7] Rudorf, *Phil. Mag.*, 1909, [vi.], **17**, 795.

[8] Onnes, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 678.

[9] Onnes, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 175.

Liquid helium has been used as a refrigerating agent in the prosecution of low temperature research at Leyden.[1]

Chemical Inertness.—Chemists generally accept the view that helium and the other members of the group are incapable of entering into chemical combination, but it may serve a purpose to collect in this place the evidence for and against this belief.

Firstly, it is of interest to know in what state helium exists in the minerals which contain it, and several investigators have, at different times, directed their efforts to the solution of this problem. At an early date it was shown[2] that when fergusonite is heated to 500°-600° C. it suddenly becomes incandescent and evolves a considerable amount of gas, which consists, as the following analysis shows, chiefly of helium:—

	Volume of Gas. c.c per Gram.	*Percentage of Total Gas.*
Helium . .	1·080	75·5 per cent
Hydrogen . . .	0·078	5·47 ,,
Carbon dioxide . .	0·245	17·14 ,,
Nitrogen . . .	0·027	1·88 ,,
Total . .	1·430	99·99 per cent.

The weight of helium evolved is 0·0326 per cent. of the weight of the mineral.

Fergusonite is a niobate of yttrium containing some uranium; it occurs in felspar and mica deposits, but it is doubtful whether it is of igneous origin or is deposited by water. It is macrocrystalline, but under the microscope shows no trace of crystalline structure, and appears to be homogeneous and free from cavities. By heating the mineral with a hydrogen flame burning in oxygen in a specially constructed calorimeter, it has been shown that the heat evolved during the change is 809 cal. per gram; moreover, the evolution of helium is accompanied by an increase of volume (a decrease might, conceivably, account for part of the heating). A similar liberation of helium with evolution of light and heat has been noticed in the case of a sample of fluor-spar containing fluorides of cerium and yttrium.[3]

Travers has pointed out, however, that many minerals which contain no helium exhibit a similar incandescence on heating,[4] and this fact rather discounts the significance of the foregoing observations.

Another fact which might be considered to point to the existence of compounds of helium in minerals is that the gas is completely eliminated from samarskite by heating in carbon dioxide, but only partially by heating in hydrogen. A similar phenomenon has been observed in the liberation of nitrogen from certain nitrides, and Kohlschutter[5] suggests that this may be due to the reduction by the hydrogen of the higher oxides which otherwise provide the oxygen required to expel the helium or nitrogen from its compounds.[1]

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[1] See Onnes, *Chem. Zeitung*, 1910, 34, 1373.

[2] Tilden, *Proc. Roy. Soc.*, 1897, 62, 325.

[3] Julius Thomsen, *Zeitsch. physikal. Chem.*, 1898, 25, 112.

[4] Travers, *Nature*, 1905, 71, 248.

[5] Kohlschutter, *Annalen*, 1901, 317, 158.

More definite conclusions may be deduced from experiments in which pitch-blende was ground *in vacuo.*[2] Helium was thus liberated in amounts which were approximately a constant proportion (1·1 to 1·2 per cent.) of the total amounts that could be obtained by heating the mineral with potassium hydrogen sulphate.

A slightly different method of attacking this problem was followed by Gray,[3] who powdered thorianite in an agate mortar, sorted the resulting powder into various grades of fineness by elutriation with water, dried the resulting fractions, and determined the amount of helium which was liberated from each on heating with nitric acid in an exhausted tube. By comparing these amounts with the total amount of helium evolved when the unground material was subjected to similar treatment with acid, it was possible to ascertain the proportion of the total helium which had been liberated by grinding to a degree of fineness which was determined in each case by microscopic examination of the powder. It appears that very little gas is liberated until the particles have a diameter as small as 10 μ; from this point the proportion of helium liberated increases with the fineness of the powder until a temporary limit is reached with particles of an average diameter of 3 μ, from which about 28 per cent. of the total helium has been given off.

Both these sets of experiments lead to the conclusion that the helium is contained in a structure (*e.g.* of cavities) which, though invisible under the microscope, is large compared with the molecular structure.

A similar conclusion is reached as the result of experiments upon the liberation of helium from monazite and thorianite by prolonged heating at various temperatures from 500°–1200°.[4] With the latter mineral there was a practical limit to the evolution of helium at any given temperature. The following are typical results:—

0·7 per cent.	of helium content liberated in	5	hours at	300°
8·5 per cent.	„ „ „	80	„ „	500°
62·3 per cent.	„ „ „	320	„ „	750°
100·0 per cent.	„ „ „	30	„ „	1000°.

It seems probable, therefore, that in thorianite, while a small proportion of the helium may be diffused throughout the mineral—possibly in solid solution—the greater part of it is concentrated in minute cavities. If this is the case, the pressure of the gas in the cavities is certainly very great; something of the order of 200 atmospheres at 0° C.[5]

It is stated that considerable amounts of helium are absorbed by the finely divided platinum produced by the so-called "electrical vaporisation"[6] of the platinum electrodes of a vacuum tube,[7] and also by magnesium electrodes in vacuum tubes, but it seems probable that this absorption, in so far as it actually exists, is a physical phenomenon, and, as the extent of the absorption was measured chiefly by the changes in the spectrum—a method which has been shown to be unreliable in the case of the inert gases[1]—too much importance must not be attached to these results.

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[1] *Cf.* Kohlschütter and Vogdt, *Ber.*, 1905, 38, 1419.

[2] Moss, *Sci. Trans. Roy. Dubl. Soc.*, 1904, [ii.], 8,

[3] Gray, *Proc. Roy. Soc.*, 1909, A, 82, 301.

[4] Orson Wood, *Proc. Roy. Soc.*, 1910, A, 84, 70.

[5] *Cf.* Travers, *Nature*, 1905, 71, 248.

[6] For a discussion of this phenomenon see Kohlschutter and Goldschmidt, *Zeitsch. Elektrochem.*, 1908, 14, 221 and 677; Fischer and Hahnel, *ibid.*, p. 366; Wolter, *ibid.*, p. 695; Kohlschütter, *ibid.*, 1909, 15, 316.

[7] Travers, *Proc. Roy. Soc.*, 1897, 60, 449.

The most exhaustive series of attempts to bring about the combination of helium with various elements and compounds was made by Ramsay and Collie.[2] A measured amount of helium was circulated over the substance at a bright-red heat; then the whole apparatus was allowed to cool, the residual helium pumped off and measured, and finally the reagent was reheated, and any gas evolved pumped off and examined. The following is a list of the reagents used:—

Sodium (distilled in the gas).
Silicon.
Glucinum.
Zinc
Cadmium } (both distilled in the gas).
Boron.
Yttrium oxide and magnesium.
Thallium.
Titanium oxide and magnesium.
Thorium oxide and magnesium.
Tin
Lead } (untarnished at red heat).

Phosphorus
Arsenic } (distilled in the gas).
Antimony
Bismuth } (unchanged).
Sulphur.
Selenium.
Uranium oxide and magnesium.
Metallic cobalt.
Platinum black (no occlusion).
Soda lime and potassium nitrate.
Soda lime and sulphur.

No change in the volume of the helium was observed in any of the experiments, and the reagent in each case appeared to be unattacked.

From experiments that have been made during the isolation of helium it is certain that it does not combine with oxygen, nitrogen, hydrogen, etc., and it has been proved that even at high temperatures it does not pass through iron or platinum and cannot, therefore, form any compound or solid solution with these elements.[3] Further, helium has no measurable solubility in solid or liquid copper, silver, gold, nickel, iron, palladium, aluminium, magnesium, uranium, or tantalum.[4]

One possibility that remains is that an endothermic compound of helium might be obtained by the action of the silent electric discharge. Berthelot stated that when helium was thus treated in presence of benzene and mercury, a green glow was seen, which gave the spectrum of mercury, and a large proportion of the gas was absorbed (68 per cent. in 210 hours) with production of a resinous solid. This solid, when heated, gave off a gas which, when purified from carbon monoxide, etc., showed exactly the same behaviour as the original gas when submitted to the discharge with benzene and mercury. Moreover, the residual gas from the first experiment could be made to undergo further contraction by the action of the discharge in presence of fresh benzene and mercury.[5]

These results are so startling that one is naturally disinclined to accept ment without confirmation, and this, hitherto, has not been forthcoming. On the other hand, Ramsay and Collie[1] submitted mixtures of helium with benzene vapour and with chlorine to the action of the silent electrical discharge for many hours, but could in no case detect any alteration in the volume of the helium or any other sign of chemical combination. Strutt also has found that helium is not absorbed when subjected to the silent discharge with benzene or carbon bisulphide.[2]

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[1] See Argon, p. 343.

[2] Ramsay and Collie, *Proc. Roy. Soc.*, 1896, 60, 53.

[3] Ramsay and Travers, *Proc. Roy. Soc.*, 1897, 61, 267; *cf.*, however, Piutti, *Le Radium*, 1911, 8, 13; it is there stated that certain minerals can absorb helium.

[4] Sieverts and Bergner, *Ber.*, 1912, 45, 2576.

[5] Berthelot, *Compt. rend.*, 1895, 120, 581, 660, 1316; 1897, 124, 118.

There appears, therefore, to be good ground for the statement that no exothermic compound of helium exists, and that neither high temperatures nor the silent discharge are capable of causing the formation of endothermic compounds of the element.

Atomic Weight.—As helium does not form any definite compound, the equivalent referred to hydrogen or oxygen cannot be determined—indeed, it cannot be said to have an equivalent. We are thus reduced to other and less satisfactory methods for the determination of its atomic weight.

Assuming the truth of Avogadro's hypothesis, it follows from determinations of the density (*supra*, p. 308) that the molecular weight of helium is 4·002 ($O_2 = 32$), and as the ratio of the specific heats is 1·66, it is probable that the atomic weight is identical with the molecular weight.

This conclusion is based (*a*) on reasoning from the assumptions of the kinetic theory of gases, from which it appears that the highest possible ratio of the specific heats—which one would expect to find in cases of the greatest molecular simplicity—is about 1·66, and (*b*) on the fact that the vapour of mercury, known on other grounds to be monatomic (*e.g.* from the vapour density), has the ratio of the specific heats, $\frac{c_p}{c_v} = 1{\cdot}66$.[3]

Confirmatory evidence of molecular simplicity is to be found in the nature of the positive rays in helium (p. 299), the Zeeman effect in helium (p. 314), the relative ranges of the α-rays of a radio-element in helium and other gases,[4] the agreement between the observed and calculated rates of production of helium from radium,[5] and in the thermal conductivity of the gas (p. 310).

The view that the atomic weight is approximately 4 receives further support from the way which helium then falls into place with the other elements of its group in the periodic classification of the elements (see Part I. Chap. VIII.).

Detection.—The simplest method for the detection of helium consists in introducing the gas into a vacuum tube connected with a side tube containing charcoal cooled in liquid air; all heavier gases are thus absorbed. In this way it was found possible to detect the helium and neon in 50 c.c. of air.[6] This method has also been used for the detection of helium in minerals.[7]

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[1] Ramsay and Collie, *loc. cit.*

[2] Strutt, *Proc. Roy. Soc.*, 1912, **A**, 87, 381.

[3] See this Vol., Part I., p. 97.

[4] E. P. Adams, *Phys. Review*, 1907, 24, 109; Taylor, *Phil. Mag.*, 1913, [vi.], 26, 402; Soddy, *Ann. Reports*, 1907, 4, 313; 1913, 10, 279.

[5] Rutherford and Geiger, *Proc. Roy. Soc.*, 1908, **A**, 81, 162; Soddy, *Ann. Reports*, 1909, 6, 234.

[6] Dewar, *Proc. Roy. Soc.*, 1899, 64, 231.

[7] Bordas, *Compt. rend.*, 1908, 146, 628; *cf.* Piutti, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii.], 15, 203; *Le Radium*, 1910, 7, 178.

CHAPTER III.

NEON (Ne).

History.—It has already been stated that after argon and helium had been discovered, there was some controversy as to their position in the periodic classification of the elements, and that the discoverers ultimately came to the conclusion that these gases must be placed by themselves in a new group. Helium then occupied the same horizontal position in the new group as lithium in Group I., while argon came next to potassium (see Part I., p. 274). A gap was thus left for an element which would occupy a position in Group 0 between argon and helium, and would have an atomic weight two or three units less than that of sodium.[1]

In the hope of discovering this gas Ramsay and Travers made a careful examination of 18 litres of argon, obtained from air in the usual manner. The gas was liquefied in a Dewar tube cooled in liquid air boiling under reduced pressure, and 25 c.c. of clear liquid were obtained; the temperature was then allowed to rise gradually and the gas that boiled off was collected in fractions.

The first fractions had a density of 14·7 (approx.), which approached that anticipated for the element between helium and argon; moreover, the spectrum of this gas was new and contained in particular a yellow line (λ 5852·65) distinct from those of sodium, helium, and krypton.[2] The colour of the light from the vacuum tube varied from fiery red to brilliant orange as the pressure fell, and the gas was absorbed by the aluminium electrodes.

When the first fraction was again cooled with liquid air it was found that a large proportion did not liquefy; this gas had a density of 9·65, but was mixed with a certain proportion of helium and argon. These impurities were removed by fractionally distilling a liquefied mixture of the original gas with a suitable proportion of oxygen; the middle fraction was freed from oxygen by passage over red-hot copper and then had a density of 10·1.

The new gas was characterised by a spectrum distinct from that of helium or argon (*vide infra*), and was named *neon* (from the Greek *νέον*, new

Toward the end of the fractionation of the original supply of liquid argon, a solid substance was obtained which distilled very slowly and could therefore be obtained in a state of considerable purity. This substance was at first supposed to be another new element, and received the name "metargon";

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[1] Ramsay and Travers, *Proc. Roy. Soc.*, 1898, 62, 316.
[2] Ramsay and Travers, *Proc. Roy. Soc.*, 1898, 63, 437.

but it was later found by Ramsay and Travers themselves that the peculiar spectrum which led to its "discovery" was probably due to argon containing a small amount of some volatile carbon compound.[1] Neon was not obtained again in the pure state until 1910 by Watson, and for this reason less is known of the properties of neon than of the other gases.

Sir J. J. Thomson, by his positive-ray method, has shown that atmospheric neon contains two kinds of atoms; one of mass 20, the ordinary neon atom, the other of mass 22 which could not be attributed to any known element. To this latter substance the name *metaneon* has been given. Attempts have been made, without success, to separate neon and metaneon by repeated fractionation over cooled charcoal, but by a series of fractional diffusions Aston has obtained a gas having a density greater than that of ordinary neon.[2] On the other hand, Leduc, who has had considerable experience in fractionating atmospheric neon from the same source as Aston's, considers it possible that the increase in density is due to the concentration of a trace of nitrogen in the end fractions.[3]

Occurrence. — Hitherto neon has been obtained only from the atmosphere. It is difficult to make an accurate determination of the amount present, but the most reliable estimate is probably that of Watson,[4] who found one volume of neon in 55,000 volumes of air.[5] Direct evidence has been obtained of the presence of neon up to considerable altitudes.[6]

Neon has also been detected in the gases from 22 thermal springs,[7] and doubtless occurs to a small extent with argon in the nitrogen present in the dissolved gases of water, in fire-damp, etc.

Collie and Patterson, working independently, have obtained evidence which points to the formation of neon and possibly traces of helium by the passage of an electrical discharge in hydrogen at low pressure. The general method of experiment consisted in introducing pure hydrogen into a vacuum tube having aluminium electrodes, passing a discharge for several hours, removing the hydrogen from the tube and exploding with excess of pure oxygen, and, finally, removing the oxygen by means of cooled charcoal, and examining the residual gas spectroscopically. In certain cases an electrodeless discharge was passed, and some of the tubes used were double-walled both with and without electrodes.

After further experiments made in collaboration, Collie and Patterson conclude that (1) neon cannot be obtained from either glass or aluminium such as that used for the tubes and electrodes by simple heating; (2) glass is not permeable to ordinary neon and helium, either when heated nearly to softening or when subject to the action of cathode rays; (3) the hydrogen and oxygen used in the experiments contained no neon. Nevertheless, they obtained spectroscopic evidence of the presence of neon in the residual gas obtained in their experiments. Masson has obtained similar results.[8]

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[1] See Ramsay and Travers, *Compt. rend.*, 1898, **126**, 1762; *Ber.*, 1898, **31**, 3111; *Proc. Roy. Soc.*, 1899, **64**, 185.

[2] Aston, *Nature*, 1913, **92**, 308; cf. *Proc. Roy. Soc.*, 1914, A, **89**, 439.

[3] Leduc, *Compt. rend.*, 1914, **158**, 864.

[4] Watson, *Trans. Chem. Soc.*, 1910, **97**, 810.

[5] *Cf.* Claude, *Compt. rend.*, 1908, **147**, 624; Bordas and Touplain, *Compt. rend.*, 1908, **147**, 591.

[6] Tesserenc de Bort, *Compt. rend.*, 1908, **147**, 219.

[7] Moureu and Biquard, *Compt. rend.*, 1906, **143**, 180; 1908, **146**, 435.

[8] Collie and Patterson, *Trans. Chem. Soc.*, 1913, **103**, 419; *Proc. Chem. Soc.*, 1913, **29**, 217; Masson, *ibid.*, p. 233; Collie, Patterson, and Masson, *Proc. Roy. Soc.*, 1914, A, **91**, 30; Collie, *ibid.*, 1914, A, **90**, 554.

Attempts made by Strutt[1] to confirm these results failed, though his apparatus enabled him to detect with ease the neon in $\frac{1}{100}$th of a c.c. of air; by his method of experiment the gases were manipulated entirely within a closed glass apparatus. Negative results have also been obtained by Merton and by Egerton.

Before the minute quantities of helium and neon observed by Collie, Patterson, and Masson can be regarded as of real significance, it is desirable that these investigators shall formulate the precise conditions under which positive results may be anticipated, and afford an explanation for the negative results that others have obtained. Certain experiments by J. J. Thomson have been cited in favour of the reality of the transmutations, but he himself states:[2] "I have never, however, been able to get any evidence, that I regard as at all conclusive, that the atom of one element could by such means be changed into an atom of a different kind."

Isolation.—(1) The earlier methods used for the isolation of pure neon all depended on the fractional distillation of liquefied mixtures of neon, argon, krypton, and xenon. That originally used by Ramsay and Travers has been outlined above.

(2) Another method used by these investigators was to take the gas escaping from the Hampson liquefier (which consists chiefly of nitrogen, together with all the more volatile constituents of air) and return it to the intake of the compression pump. It was thus again partially liquefied, and deprived of a further proportion of its less volatile constituents, and a gas was ultimately obtained comparatively rich in helium and neon. This concentration of the lighter gases could also be brought about by liquefying the whole of the gas escaping from the air liquefier and blowing a current of air through the liquid; the portion that first evaporated contained most of the helium and neon present.

The enriched gas was next freed from oxygen and nitrogen by the usual chemical methods, and the residue was again liquefied and fractionated to remove argon. Finally, neon was separated from helium by cooling the mixture to the temperature of liquid hydrogen and pumping off the still gaseous helium from the solid neon.[3]

(3) A simpler method for separating neon from the mixture of inert gases obtained from air depends on the use of cooled charcoal in the manner devised by Dewar (see p. 306). It is found that when the mixture is brought in contact with charcoal cooled to about − 100° C., the argon, krypton, and xenon are completely absorbed, while the greater part of the helium and neon can be pumped away in the gaseous state. The neon can then be separated from helium by bringing the gas in contact with charcoal cooled to the temperature of liquid air (− 180° to − 190° C.); the neon is largely absorbed, while all the helium with a little of the neon can be pumped off. When the charcoal is allowed to warm up to the ordinary temperature, the neon is evolved in a fairly pure state.[4]

From the gas retained in the first lot of charcoal, krypton and xenon can be obtained (see p. 347).

(4) The most convenient method of obtaining neon from the air is by

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[1] Strutt, *Proc. Roy. Soc.*, 1914, A, 89, 499; Merton, *ibid.*, 1914, A, 90, 549; Egerton, *ibid.*, 1915, A, 91, 180.

[2] J. J. Thomson, *Nature*, 1913, 90, 645; *The Romanes Lecture*, 1914, p. 18.

[3] Ramsay and Travers, *Proc. Roy. Soc.*, 1901, 67, 329; Dewar, *ibid.*, 1901, 68, 362.

[4] Valentiner and Schmidt, *Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 38, 816; Moureu and Biquard, *Compt. rend.*, 1906, 143, 180.

means of a modification of Claude's apparatus for the fractional condensation and distillation of liquid air, which is depicted diagrammatically in fig. 86.

Cooled air under pressure is introduced into the vessel A and ascends the

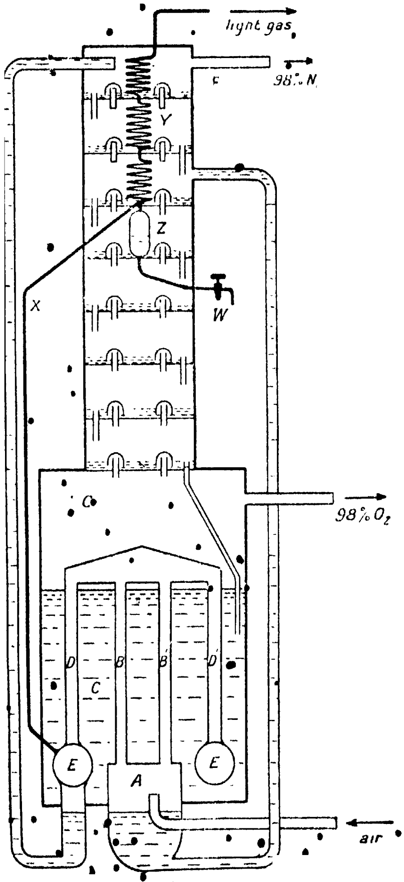

FIG. 86

tubes BB′, which are cooled in a bath of liquid oxygen. Here the greater part of the oxygen and some nitrogen are condensed, and the liquid falls back into the reservoir A. The gas next passes down other tubes DD′, which are also surrounded by the liquid oxygen, and here the nitrogen is condensed almost completely, and collects in the reservoir E.

The upper part of the apparatus consists of a rectifying column, similar in construction to that of Coffey's still. By the pressure of gas in the tubes the liquid in the reservoir A is forced up the tube t_1 and delivered into the column at a point a little below the top, while the liquid in E is similarly forced to the top of the column through the tube t_2.

The oxygen in C is at its boiling-point under atmospheric pressure, and the highest temperature is found in this liquid and at the bottom of the rectifying column. On the other hand, the liquid in E when suddenly placed under atmospheric pressure at the top of the column, boils rapidly, losing the greater part of its nitrogen and producing the lowest temperature found in any part of the apparatus. As the liquid passes down the column it becomes steadily warmer, and meets a current of gas which becomes steadily cooler as it ascends. The net result of these heat interchanges is that practically all the oxygen in the ascending gas is liquefied and drops back into C, while all the nitrogen in the descending liquid is distilled off, and passes out into the atmosphere at F.

This description of the apparatus and its working is necessary in order to make clear the nature of the modification by which the helium and neon present in the air can be obtained. It will be evident that, as these gases have extremely low boiling-points, they will remain as gas in the space above the liquid in E. A narrow tube X is therefore provided, by which these uncondensed gases are led up to the top of the column, where they pass through the spirals Y, situated at the point where the temperature is lowest (*vide supra*). Here a great part of the residual nitrogen is condensed and falls back into the small reservoir Z, from which it is blown off from time to time through the cock W.

When the flow of gas and liquid in the various parts of the apparatus is suitably adjusted, the residual gas escaping from the top of the small spirals contains all the helium, neon, and hydrogen present in the air delivered into the apparatus, together with about 50 per cent. of nitrogen.[1]

From the crude light gas obtained by this method the nitrogen may be at once removed by the ordinary chemical methods (see Argon), but a simpler plan is to fractionate the whole over cooled charcoal repeatedly. The nitrogen is absorbed most readily, the neon less readily, and the helium hardly at all at the temperatures used. A saving of time, however, may be effected if after several fractionations have been made, the nitrogen is absorbed by chemical methods. The progress of the purification is best followed by means of determinations of density: spectroscopic examination is almost useless, as large quantities of helium may escape detection.[2]

It will be evident from the above descriptions that neon is the most difficult of the inert gases to isolate. This is due partly to the extremely minute proportion present in the air, the only available source, and also to the fact that it has to be isolated from the middle fractions of the inert gas, in which purity is more difficult to attain than in end fractions.

Evidence of the homogeneity of neon has been obtained by the observation that its vapour pressure is unchanged during the fractional distillation of the liquefied gas.[3] Quartz at 1000° C. is permeable to neon, but much less so than to helium.[4]

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[1] See this Vol., Part I., p. 41; Claude, *Compt. rend.*, 1905, **141**, 823; 1908, **147**, 624.
[2] Watson, *Trans. Chem. Soc.*, 1910, 97, 810.
[3] Travers, Senter, and Jaquerod, *Phil. Trans.*, 1903, **200**, A, 131.
[4] O. W. Richardson and Ditto, *Phil. Mag.*, 1911, [vi.], **22**, 704.

Properties.—The *density* of neon has been determined by Watson[1] using a sample of the gas prepared by method (4) above. He found 0·9002 gm. ± 0·0003 gm. for the weight of the normal litre, which corresponds to a density of 20·16 ($O_2 = 32$). Ramsay and Travers had previously found the value 19·94 ($O_2 = 32$),[2] but the later determination is undoubtedly more accurate. Leduc gives 0·899 gm. as the weight of a normal litre.[3]

From Watson's value for the density, and Burt's value given below for the pressure compressibility coefficient, it follows from the method of limiting densities that the molecular weight of neon is **20·20**.

The *compressibility coefficient* of neon at 0° between 0 and 1 atmosphere is, according to Burt, – 0·00105; that is, neon, like hydrogen, is an ultra-perfect gas.[4] Leduc's value is – 0·00046 at 17°.[3] The *thermal conductivity*[5] is 0·0001091 c.g.s. units at 0° C., and the temperature coefficient 0·00259.

The *refractivity* of neon was given by Ramsay and Travers as 0·2345 times that of air for white light, whence the refractive index is = 1·0000687.[2] This figure agrees fairly well with that found by C. and M. Cuthbertson,[6] namely, 1·00006716 at 0° and 760 mm. for the green mercury line (λ = 5461.).

The *dispersion* at N.T.P. is approximately twice that of helium, the relationship between wave-length and refractive index being given by

$$\mu - 1 = \frac{C}{n_0^2 - n^2}$$

where $C \times 10^{-27} = 5{\cdot}18652$ and $n_0^2 \times 10^{-27} = 38916{\cdot}2$.

The *absorption coefficient* of neon in water is 0·0114 at 0°, and increases gradually up to 0·0317 at 50°. The solubility curve appears to have a minimum at 0°.[7]

The *viscosity* of neon at 0° C. is $2{\cdot}981 \times 10^{-4}$ in absolute units.[8]

The *dielectric cohesion* of pure neon at 17° is 5·6 (hydrogen = 205), which is considerably less than that of helium, whereas one would expect it to be between that of helium and argon. The value of the dielectric cohesion is very much raised even by traces of foreign gases; *e.g.* 1/20th per cent. of impurity raises it to 6·8, and the determination of this constant therefore affords a good criterion of the purity of the gas.[9]

When an electrical discharge is passed through neon under reduced pressure a brilliant orange-pink light is emitted.[2] The *spectrum* is characterised by lines in the orange and red regions and, like that of helium, argon, krypton, and xenon, is materially altered by inclusion of a Leyden jar and spark-gap, the strongest of the ordinary lines being only just visible, while many new lines appear in the more refrangible region.[10]

The chief lines are enumerated below[11]:—

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[1] Watson, *Trans. Chem. Soc.*, 1910, 97, 826.

[2] Ramsay and Travers, *Proc. Roy. Soc.*, 1901, 67, 329.

[3] Leduc, *Compt. rend.*, 1914, 158, 864.

[4] Burt, *Trans. Faraday Soc.*, 1910, 6, 19. See also Onnes and Crommelin, *Proc. K. Akad. Wetensch. Amsterdam*, 1915, 18, 515.

[5] Bannawitz, *Ann. Physik*, 1915, [iv.], 48, 577.

[6] C. and M. Cuthbertson, *Proc. Roy. Soc.*, 1910, A, 83, 149; 1910, A, 84, 13.

[7] Antropoff, *Proc. Roy. Soc.*, 1910, A, 83, 474.

[8] Rankine, *Proc. Roy. Soc.*, 1910, A, 83, 516; A, 84, 181.

[9] Bouty, *Compt. rend.*, 1910, 150, 149, 1380; *Ann. Chim. Phys.*, 1911, [viii.], 23, 5; [viii.], 28, 545.

[10] Merton, *Proc. Roy. Soc.*, 1914, A, 89, 447.

[11] Baly, *Proc. Roy. Soc.*, 1903, 72, 85

Wave-Length.	*Intensity.*	*Wave-Length.*	*Intensity.*	*Wave-Length.*	*Intensity.*
6402·40	10	6163·79	10	5974·73	6
6383·15	8	6143·28	10	5944·91	10
6328·88	6	6128·63	8	5882·04	8
6304·99	8	6096·37	10	5852·65	20
6266·66	10	6074·52	10	5764·54	8
6217·50	8	6030·20	10	4259·53	6
6182·37	10	5975·78	8	...	...

An investigation of three series of lines in the neon spectrum has been made by Rossi.[1]

The *Zeeman effect* in neon is very complicated.[2]

A curious property of neon has been observed by Collie.[3] When the gas is shaken in a tube with mercury a red glow is observed which is equally bright at atmospheric pressure or at 120–200 mm. By unequal heating and other methods tubes were obtained which would glow at certain parts but not at others. Moisture inhibits the phenomenon.[4]

No explanation appears to have been advanced: possibly it may be connected with the glow seen in an exhausted receiver containing neon moving near an electrostatic field.[5] It is stated that neon is very resistant to absorption by the electrodes of a discharge tube.[6]

The minimum spark potential in neon is 200 volts, with a spark-gap of 2·8 mm.[7]

The earlier investigators had not sufficient neon at their disposal to permit the determination of the ratio of the specific heats; but from the fact that mixtures of neon with argon were already known to have $\gamma = 1·66$, it was concluded that the value of γ for neon was that required by theory for a monatomic gas.[8] Subsequently accurate determinations of this constant have been made for pure neon according to the method of Kundt and Warburg (see p. 316): the figures obtained are[9]:—

	Temperature.	*Half Wave-Length.*	*Density.*
Air . . .	19°	27·92	14·48
Neon . . .	19°·4	36·10	10·1

The value thus found for the ratio C_p/C_v for neon is 1·642.

Liquefaction of Neon.—Neon can be liquefied under the ordinary atmospheric pressure at the temperature of liquid hydrogen boiling under ordinary conditions.[1]

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[1] Rossi, *Phil. Mag.*, 1913, [vi.], 26, 981; *cf.* Watson, *Proc. Roy. Soc.*, 1908, A, 81, 181; *Astrophys. J.*, 1911, 33, 399.

[2] Lohmann, *Zeitsch. Wiss. Photochem.*, 1908, 6, 1, 41.

[3] Collie, *Proc. Roy. Soc.*, 1909, A, 82, 378.

[4] *Cf.* Claude, *Compt. rend.*, 1910, 151, 1122.

[5] Jervis-Smith, *Proc. Roy. Soc.*, 1908, A, 81, 430.

[6] Claude, *Compt. rend.*, 1913, 156, 1317.

[7] Watson, *Proc. Camb. Phil. Soc.*, 1913, 17, 90.

[8] Ramsay and Travers, *Proc. Roy. Soc.*, 1901, 67, 329.

[9] Ramsay, *Proc. Roy. Soc.*, 1912, A, 86, 100.

Its boiling point[4] is $-245^\circ{\cdot}92$ C. The vapour pressure of liquid neon rises from 32·35 cm. at $-248^\circ{\cdot}67$ C. (the triple point) to 81·52 cm. at $-245^\circ{\cdot}68$ C.[4] Two results at still lower temperatures have been recorded,[2] namely, 12·8 mm. at $-252^\circ{\cdot}6$ C. and 2·4 mm. at $-257^\circ{\cdot}35$ C.

Its triple-point pressure is 35 cm. of mercury, and its critical pressure is 29 atmospheres; but the critical temperature has not been determined. There is, however, a connection between the critical temperatures and the viscosities of the inert gases. The variation of η with T is expressed by Sutherland's equation:—

$$\eta = \eta_0\left(\frac{T}{T_0}\right)^{\frac{2}{3}}\left(\frac{C+T_0}{C+T}\right)$$

where η and η_0 are the viscosities at temperatures T° and T_0° abs., and C is a constant for each gas.

When the values of η at the critical temperature are calculated for the other inert gases, it is found that the relationship $\eta_k^2 = 3{\cdot}93 \times 10^{-10} \times$ at. wt. holds good. By interpolation the value of η_k and hence, by Sutherland's equation, of T_k for neon may be found to be 61°·1 absolute.[3] This value agrees with that suggested by Travers, Senter, and Jaquerod (*loc. cit.*), viz. 60° abs. According to Onnes and Crommelin,[4] the critical temperature of neon is approximately 42° to 45° absolute.

The surface tension, density, and refractive index of liquid neon have not yet been measured; but Rudorf calculates that its refractive index should be about 1·24.[5]

Atomic Weight.—The atomic weight of neon is believed to be identical with its molecular weight, which is, as has already been mentioned, taken as 20·20. The reasons for this belief may be summarised briefly as follows:—

(1) The ratio of the specific heats at constant pressure and constant volume is 1·64;

(2) The gas has an extremely small dielectric cohesion (*cf.* Helium, p. 312, and Argon, p. 339);

(3) The evidence of the positive-ray method (p. 295).

(4) The general relationship of the element to the other inert gases and to other elements indicates that it should properly occupy the position in the periodic classification between fluorine and sodium into which it naturally falls if its atomic weight is taken as 20·20.

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[1] Dewar, *Proc. Roy. Soc.*, 1901, **68**, 360; Ramsay and Travers, *ibid.*, 1901, **67**, 329; Travers, Senter, and Jaquerod, *ibid.*, 1902, **70**, 484; *Phil. Trans.*, 1903, **200**, A, 131.

[2] Travers, Senter, and Jaquerod, *loc. cit.*

[3] Rankine, *Phil. Mag.*, 1911, [vi.], **21**, 49.

[4] Onnes and Crommelin, *Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 15. See also 1911, **14**, 165.

[5] Rudorf, *Phil. Mag.*, 1909, [vi.], **17**, 795.

CHAPTER IV.

ARGON (A).

History.—A curious example of the omissions that sometimes come to light during the investigation of common substances is found in the fact that from 1785 till 1894 no complete and exhaustive examination of the homogeneity of atmospheric nitrogen was attempted. In the former year Cavendish published his *Experiments on Air*, in which he investigated this point as minutely as his methods and apparatus would permit; but that he recognised his own limitations is evident from the following sentence written at the conclusion of his paper: ". . . if there is any part of the phlogisticated air of our atmosphere which differs from the rest, and cannot be reduced to nitrous acid, we may safely conclude that it is not more than $\frac{1}{120}$th part of the whole."[1]

This observation remained unnoticed until Rayleigh, in the course of a very accurate determination of the density of nitrogen from various sources, observed that the density of atmospheric nitrogen, by whatever method obtained, was consistently higher than that of "chemical" nitrogen, obtained from ammonia, oxides of nitrogen, etc. This discrepancy (amounting to $\frac{1}{130}$th of the whole) was much too great to be written off as experimental error, as may be seen from the data quoted below, in which the error of the determination does not exceed 0·0002 gm.

	Weight of Gas in Large Globe.
I. Nitrogen from .—	
Nitric oxide by red-hot iron (4 expts.)	2·30008 gms.
Nitrous oxide by red-hot iron (2 expts.)	2·29904 ,,
Ammonium nitrite; purified at red-heat (2 expts.) .	2·29869 ,,
Ammonium nitrite; purified cold	2·29870 ,,
Urea and sodium hypobromite	2·2985 ,,
II. Nitrogen from air:—	
By means of red-hot copper (1892)	2·31026 ,,
By means of red-hot iron (1893) (4 expts.) . .	2·31003 ,,
By means of cold ferrous hydroxide (1894) (3 expts.)	2·31020 ,,

Mean of Series I. = 2·29927 gms.
Mean of Series II. = 2·31016 ,,

Difference = 0·01089 gm.

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[1] Cavendish, *Phil. Trans.*, 1785, 75, 372.

Rayleigh proved that the density of none of these specimens was altered by the action of the silent electrical discharge, and demonstrated, moreover, that the lightness of "chemical" nitrogen was not due to admixture with any known gas lighter than itself, such as hydrogen, ammonia, or water vapour.[1]

The only other possible explanation of the high density of "atmospheric" nitrogen was the presence in it of some heavier constituent. It was at this point that a search in the literature revealed the astounding fact that the accepted view as to the homogeneity of the nitrogen of the air rested solely upon the experiments of Cavendish mentioned above. It was at once evident that, if his small residue were a gas having a density double that of nitrogen, its presence would more than suffice to account for the observed differences.

Cavendish had passed sparks from an electrical machine through a mixture of air with excess of oxygen (dephlogisticated air) over mercury, and had afterwards absorbed the excess of oxygen and oxides of nitrogen by means of liver of sulphur. Repetition of the experiments with improved apparatus demonstrated that a residue was *always* obtained, and that its volume was proportional to the volume of air used. Spectroscopic examination proved conclusively that it was not nitrogen.

In collaboration with Ramsay, Rayleigh then obtained this new gas from air by absorbing the oxygen and nitrogen by the action of red-hot copper and magnesium respectively, and it was shown by spectroscopic examination to be identical with the gas obtained by Cavendish's method. That the new gas was not combined with the nitrogen was proved by its separation by atmolysis.

This new gas had a density of about 20 (H = 1), whence its molecular weight would be about 40. The high ratio of the specific heats pointed to the conclusion that its molecule was monatomic, *i.e.*, that its atomic weight was also 40. To this new element the name *argon* (ἀργόν, inactive) was given.[2]

At first it did not seem as if there could be any place in the periodic classification for an element of atomic weight 40, but as time went on and other members of the group described in this volume became known, chemists generally accepted the view, first suggested by Ramsay, that argon should be placed in a new group of the periodic system between bromine and potassium. By allocating this position to argon there arises an anomaly which is even now unexplained, as its atomic weight is greater than that of potassium which it precedes, but the greater part of the available evidence goes to justify the accepted view.

Occurrence.—Argon is widely distributed in the free state in nature. As has already been mentioned, it is a constant constituent of the atmosphere. It forms 0·941 per cent. by volume of air freed from carbon dioxide and moisture,[3] and 1·1845 per cent. by volume of atmospheric "nitrogen."[3] The substantial accuracy of these figures has been verified by calculating the density of atmospheric nitrogen from them in conjunction with the known densities of pure argon and nitrogen. Results are thus obtained which agree closely with the values found experimentally by Rayleigh.[4]

The proportion of argon in the air appears to be constant, as samples taken from places as widely separated as Berlin, London, and Paris, and at heights varying from 0–5800 metres, contained amounts of argon varying between 0·932 and 0·935 per cent. by volume.[1] Over the open sea, however, slightly higher proportions (up to 0·949 per cent.) have been found.[2]

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[1] Rayleigh, *Proc. Roy. Soc.*, 1893, 53, 146; 1894, 55, 340.

[2] Rayleigh and Ramsay, *Phil. Trans.*, 1895, 186, 187.

[3] Schloesing, *Compt. rend.*, 1895, 121, 605; Kellas, *Proc. Roy. Soc.*, 1895, 59, [illegible]

[4] Ramsay, *Proc. Roy. Soc.*, 1899, 64, 181.

From the air argon finds its way into sea and river water,[3] and because its solubility in water is greater than that of nitrogen, its proportion in the total dissolved gas is greater than in air. This greater solubility of argon will also explain why the proportion of argon in the gases from the air-bladders of fishes is alway higher than in air and increases with the depth from which the fish is taken,[4] and will account for the low proportion of argon in air taken from the soil.[5] It has been found free in plants,[6] and occurs in the blood of animals,[7] but not in combination.[8]

Argon has been found in the gas from the fumaroles of Mount Pelée (Martinique) and of Guadeloupe.[9] It also occurs in the gases of many mineral springs, among which may be enumerated Wildbad, Black Forest;[10] Perchtoldsdorf, Vienna;[11] Reyjavik, Iceland;[12] Allhusen's Well;[13] Bath and Buxton;[13] Old Sulphur Well, Harrogate; Strathpeffer Wells; Des Œufs, César and Espagnol Springs at Cauterets;[14] Vöslau;[15] Monte Irone, Abano; Larderello, Tuscany; Poretta Baths, Bolognian Appenines;[16] Mount Doré;[17] Peyré, Ogen; Nehe and Trou des Pauvres, Dax; Vielle, Eaux Bonnes; Saint Augustin, Panticosa;[18] Maizières, Côte d'Or;[19] Raillère, Pyrenees;[20] Bagnoles de l'Orne (4·5 per cent.).[21]

Argon has been found in the natural gas of Kentucky (see p. 302), and in many specimens of fire-damp,[22] in amounts which vary from 0·6 to 0·04 per cent. of the whole volume, but in almost every case are about 2 per cent. by volume of the nitrogen present.

If we now review the modes of occurrence of argon which have been enumerated, it will be found that in every case the gas occurs associated with nitrogen in proportions which are approximately of the same relative magnitude as the proportions of argon and nitrogen in the atmosphere.

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[1] Schloesing, *Compt. rend.*, 1896, **123**, 696.
[2] Moissan, *Compt. rend.*, 1903, **137**, 600.
[3] Troost and Ouvrard, *Compt. rend.*, 1895, **121**, 798.
[4] Schloesing and Richard, *Compt. rend.*, 1896, **122**, 615.
[5] Schloesing, *Compt. rend.*, 1895, **121**, 604.
[6] Tolomei, *Chem. Zentr.*, 1897, [i.], 1030.
[7] Regnard and Schloesing, *Compt. rend.*, 1897, **124**, 302.
[8] Zaleski, *Ber.*, 1897, **30**, 965.
[9] Moissan, *Compt. rend.*, 1902, **135**, 1085; 1904, **138**, 936; *Bull. Soc. chim.*, 1903, [iii.], **29**, 434.
[10] Kayser, *Chem. News*, 1895, **72**, 89.
[11] Bamberger, *Monatsh.*, 1896, **17**, 604.
[12] Kellas and Ramsay, *Proc. Roy. Soc.*, 1895, **59**, 68.
[13] Friedländer, *Zeitsch. physikal. Chem.*, 1896, **19**, 657; Rayleigh, *Proc. Roy. Soc.*, 1896, **60**, 56; 1897, **62**, 198.
[14] Ramsay and Travers, *Proc. Roy. Soc.*, 1897, **60**, 442.
[15] Bamberger and Landsiedl, *Monatsh.*, 1898, **19**, 114.
[16] Nasini, Anderlini and Salvadori, *Gazzetta*, 1898, **28**, i. 81.
[17] Parmentier and Hurion, *Compt. rend.*, 1900, **130**, 1190.
[18] Moureu, *Compt. rend.*, 1902, **135**, 1335.
[19] Moureu, *Compt. rend.*, 1895, **121**, 819.
[20] Bouchard, *Compt. rend.*, 1895, **121**, 392. See also for summary, Moureu, *Compt. rend.*, 1906, **142**, 1155.
[21] Bouchard and Desgrez, *Compt. rend.*, 1896, **123**, 969.
[22] Schloesing, *Compt. rend.*, 1896, **122**, 398; 1896, **123**, 233; 1896, **123**, 302.

For example, brine from the rock-salt beds near Middlesbrough effervesces when it reaches the surface and gives off a gas which contains 98 per cent. of nitrogen.[4] This "nitrogen" contains about 1·24 per cent. of argon, or about the same proportion as is contained in atmospheric nitrogen.[1] It seems, therefore, probable that in all such cases the argon has been derived indirectly from the atmosphere.[2]

It appears to be generally assumed that the atmospheric argon has existed in the elementary state since the earliest stages of the world's history. But few minerals have been found hitherto which yield argon on heating: of these the chief are *malacone*,[3] and another mineral from Brazil.[4] It is noteworthy that both minerals contain large amounts of zirconium (malacone has the formula $3(ZrO_2.SiO_2).H_2O$, and the Brazilian mineral contains 97 per cent. ZrO_2), and both are radioactive. Further, it is held by Antropoff[5] that the amount of argon in the second mineral is too great to be derived from atmospheric sources. There is, therefore, at least a basis for the speculation that argon, like helium, may be a product of the disintegration of radioactive elements, but it must be borne in mind that the amount of argon present is quite small.

Argon has also been found in *eliastite*,[6] and in a cerium mineral from Gov. Batum (South Caucasus).[7]

Isolation.—Argon is always obtained from atmospheric nitrogen. By the removal of oxygen and nitrogen from air freed from carbon dioxide, etc., we obtain "atmospheric argon," in which the only impurities are small traces of the other inert gases, helium, neon, krypton, and xenon, amounting in all to about 0·25 per cent., by volume.

The chief methods used for "atmospheric argon" are as follows:—

(1) Cavendish's original experiment has been developed and modified by Rayleigh and Ramsay,[8] whose apparatus is represented diagrammatically in fig. 87.

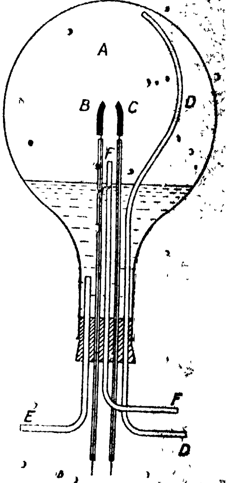

Fig. 87.—Rayleigh and Ramsay's modification of Cavendish's apparatus.

The glass flask A, having a capacity of about 50 litres, is supported mouth downwards in a suitable stand. It is closed by a rubber bung through which pass five tubes. Two of these carry heavy copper leads which terminate above in the electrodes B, C, constructed of heavy platinum rod. The bent tube D delivers soda solution against the top of the flask so that it runs down over the whole interior surface of the flask and away through the exit pipe E: the liquid is kept in circulation by a small iron centrifugal pump, and at one point passes through a worm cooled externally with water. The mixture of 11 volumes of oxygen and 9 volumes of air is supplied through the tube B.

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[1] Bedson and Shaw, *Proc. Chem. Soc.*, 1895, 11, 143.

[2] For a fuller development of this argument see Walter, *Physikal. Zeitsch.*, 1911, 12, 178.

[3] Ramsay and Travers, *Proc. Roy. Soc.*, 1897, 60, 442; Kitchin and Winterson, *Trans. Chem. Soc.*, 1906, 89, 1568.

[4] Antropoff, *Zeitsch. Elektrochem.*, 1908, 14, 585.

[5] Antropoff, *ibid.*, 1909, 15, 144.

[6] Lockyer, *Proc. Roy. Soc.*, 1896, 60, 133.

[7] Tschernik, *J. Russ. Phys. Chem. Soc.*, 1897, 29, 291

[8] Rayleigh and Ramsay, *Trans. Chem. Soc.*, 1897, 71,

In order to maintain between the electrodes the potential difference required to give a steady flame, it is necessary to use a transformer or induction coil which will give a P.D. of 6000 to 8000 volts on open secondary circuit. This falls to about 2000 in working, but a transformer giving only this voltage, or even 4000–5000 volts, on open secondary circuit will give unsteady conditions in use and probably lead to overheating and fusion of the electrodes. It is, however, necessary to the efficiency of the process that the electrodes should be kept red hot.

The primary current is regulated by means of a choking-coil with a movable iron armature, and is about 40 amps. at 30 volts. The rate of consumption of energy is about 800 watts, *i.e.* 1 h.p. roughly; and the rate of absorption of gas is about 20 litres per hour (25 c.c. per watt-hour), which may, by paying careful attention to the composition of the gases, be maintained until the amount of argon in the globe is sufficient to dilute the gases considerably.

Contrary to expectation, increase of pressure does not materially increase the rate of combination; but it has been found that with approximately the same size of flame the absorption increases rapidly with increase in the size of the globe.

This process can be pushed to completion and a mixture of argon and oxygen obtained, from which the latter gas is removed by alkaline pyrogallol, cuprammonium solution, or red-hot copper; but it is found better to use it only for the preliminary concentration of argon and to complete the removal of nitrogen by one of the other methods.[1]

(2) When nitrogen is passed over red-hot magnesium it is absorbed with formation of magnesium nitride, Mg_3N_2, and it was by systematic repetition of this process that Ramsay first obtained argon from atmospheric "nitrogen."[2] It has the disadvantage, however, of being extremely slow, and it was early suggested that other metals which more readily form nitrides should be substituted for the magnesium; chief of these were lithium, obtained by electrolysis of the chloride;[3] and barium, prepared by the action of sodium on barium fluoride or $BaNa_2F_4$.[4]

A very rapid method and the best available for some years is also a modification of the original magnesium method, due to Maquenne. The absorbent is a mixture of 5 parts of lime, which should be free from carbonate and hydroxide, and 3 parts of magnesium powder;[5] and the addition of a small proportion of metallic sodium is stated to increase the rate of absorption.[6]

The mixture is heated to bright redness in a glass tube, any hydrogen or carbon monoxide evolved being pumped off. Atmospheric "nitrogen", i then admitted, and the absorption of the nitrogen is evidenced by a glow which passes along the tube as the mixture becomes converted into calcium nitride. The gas issuing from the tube is freed from traces of hydrogen and carbon monoxide by passage over red-hot copper oxide and solid caustic potash, and is finally dried by means of phosphorus pentoxide.

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[1] Rayleigh, *Proc. Chem. Soc.*, 1897, **13**, 16.

[2] Ramsay, *Phil. Trans.*, 1895, **186**, 200.

[3] Guntz, *Compt. rend.*, 1895, **120**, 777.

[4] Limb, *Compt. rend.*, 1895, **121**, 887.

[5] Maquenne, *Compt. rend.*, 1895, **121**, 1147.

[6] Crommelin, *Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 54; see also Carracido, *Anal. Fis. Quim.*, 1909, **7**, 109.

For the removal of the last traces of nitrogen, red-hot crystallised calcium has been used;[1] and the same end is attained by maintaining an electric arc between calcium electrodes in the gas for twenty-four hours.[2]

(3) A method for preparing argon which appears to be cheap and effective is that due to Fischer and Ringe. A mixture of 90 per cent. of calcium carbide and 10 per cent. of calcium chloride, heated to redness in an iron retort of the form shown in fig. 88, having the open end water-jacketed and fitted with a water-cooled stopper, is used to absorb the oxygen and nitrogen from air.

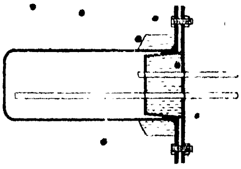

FIG. 88.

The retort is made part of a system of apparatus indicated in the diagram (fig. 89).

In an experiment the retort is first warmed and the contained gases are pumped out; the temperature is then raised to 800°, air is admitted, and when the oxygen and nitrogen have been absorbed, more air is admitted from time to time to compensate for this absorption. When the whole apparatus is full of impure argon the gas is circulated through the system until no further absorption is indicated by the manometer.

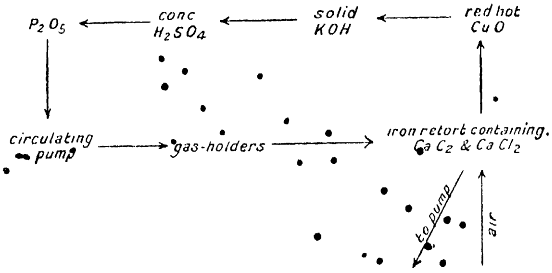

FIG. 89.

The chemical changes which take place are as follows:—nitrogen acts upon calcium carbide to form calcium cyanamide and carbon, the carbon unites with oxygen to form carbon dioxide (which is absorbed by the calcium carbide with formation of calcium carbonate and carbon), and some carbon monoxide which in turn is oxidised by the copper oxide to carbon dioxide and absorbed by the potash.

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[1] Moissan and Rigaut, *Compt. rend.*, 1903, 137, 773; *Ann. Chim. Phys.*, 1904, [viii.], 2, 433; Fischer and Hahnel, *Ber.*, 1910, 43, 1435; Guntz and Basset, *Bull. Soc. Chim.*, 1906, [3], 35, 404.

[2] Fischer and Iliovici, *Ber.*, 1909, 42, 527.

Eleven litres of fairly pure argon were thus obtained in two days by the use of 7 kilos of calcium carbide.[1]

(4) A good method for the laboratory preparation of small amounts of argon depends on the fact that commercial compressed oxygen, prepared by fractional distillation of liquid air, contains over 3 per cent. of argon and but little nitrogen. If the oxygen be removed by means of red-hot iron or copper and the residual gas freed from nitrogen by one of the above methods, a fairly pure sample of argon is readily obtained.[2]

The argon obtained by any of the above methods always contains a small proportion of the other inert gases (0·25 per cent., of which the greater part is neon) which cannot, of course, be removed by chemical methods. The isolation of pure argon from the mixture may be carried out by one of the following methods:—

(1) Fractional diffusion.
(2) Fractional liquefaction of the gas or fractional distillation of the liquid.
(3) Fractional crystallisation of the liquid.
(4) Fractional absorption in cooled charcoal.

Of these (1) is too slow and troublesome to be of much practical use, and (3) presents great experimental difficulties, and has only been carried out for the accurate determination of the atomic weight (*q.v.*). Both the other methods, (2) and (4), are good, but (2) is perhaps the simpler: it is quite easy to separate argon from helium and neon, on the one hand, and from xenon and krypton, on the other, by fractional distillation at the temperature of liquid oxygen.[3]

Physical Properties.—Argon, like the other members of the group, is a colourless, odourless, tasteless gas.

Many determinations of its *density* have been made; the more important results are tabulated below (referred to $O_2 = 32$):—

(*a*) 19·940,[4] (*b*) 19·957,[5] (*c*) 19·945,[6] (*d*) 19·95,[7] (*e*) 19·9728.[8]

(*a*) This result is the mean of a number of density determinations made on "atmospheric argon" containing all the helium, neon, etc., present in the original air. The second figure (*b*) is for the middle fractions obtained in the evaporation of liquefied atmospheric argon, whilst the third (*c*) is a more recent determination made on material similarly prepared. The fourth figure (*d*) was obtained with argon purified by fractional crystallisation, and identical results were obtained with the samples of gas taken from the solid and liquid fractions. The fifth (*e*) was obtained with spectroscopically pure gas. The accepted figure for the density of argon is 19·95, *i.e.* the weight of a normal litre of argon is 1·782 grams. Schultze gives the value 1·78376 grams, and, by the method of limiting densities, finds that the molecular weight is 39·945.

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[1] Fischer and Ringe, *Ber.*, 1908, 41, 2017; Fischer, *Zeitsch. Elektrochem.*, 1907, 13, 107; *Ber.*, 1907, 40, 1110; Crofts, *Trans. Chem. Soc.*, 1915, 107, 305.

[2] Claude, *Compt. rend.*, 1910, 151, 752; *see also*, Morey, *J. Amer. Chem. Soc.*, 1912, 34, 491; Stark, *Physikal. Zeitsch.*, 1913, 14, 497.

[3] Crommelin, *Proc. K. Akad. Wetensch. Amsterdam*, 1910, 13, 54.

[4] Rayleigh and Ramsay, *Phil. Trans.*, 1895, 186, 187; Rayleigh, *Proc. Roy. Soc.*, 1896, 59, 198.

[5] Ramsay, *Ber.*, 1898, 31, 3111; Ramsay and Travers, *Proc. Roy. Soc.*, 1899, 64, 183.

[6] Fischer and Hahnel, *Ber.*, 1910, 43, 1435.

[7] Fischer and Froboese, *Ber.*, 1911, 44, 92.

[8] Schultze, *Ann. Physik*, 1915, [iv.], 48, 269.

Argon, like helium, expands normally with increase of temperature from 0° to 280°: its coefficient of expansion is 0·003668.[1]

The *pv* isothermals for the gas between − 150° and + 20° and the reduced equation of state have been studied by Onnes and Crommelin.[2] The compressibility coefficient of the gas at 0° C. and between 0 and 1 atmosphere has been calculated by Watson to be + 0·00093.[3]

The *solubility* of argon in water is about 2½ times that of nitrogen—roughly 4 vols. per 100 vols. of water at ordinary temperatures.[4]

The absorption coefficient, measured according to the method of Estreicher, is 0·0561 at 0° and 0·02567 at 50°, and appears to show a steady fall with rise of temperature.[5] Fox has shown, however, that these results may be in error by as much as 5 per cent.,[6] and greater weight must therefore be attached to the determinations of Antropoff,[7] which give for the solubility coefficient the values 0·0561 at 0°, 0·0379 at 20°, and 0·0343 at 50°: the results show a distinct minimum at 40°.

Argon does not conform strictly to Graham's Law, but diffuses through a minute hole in a platinum plate 3½ per cent. faster than would be anticipated when compared with oxygen. This behaviour may be explained by taking into account the high ratio of the specific heats.[8] Argon diffuses through a caoutchouc membrane 100 times as fast as carbon dioxide.[9]

The *viscosity* of argon is high—about 1·21 times that of air[10]—and in respect of this property it heads the list of the principal gases. The coefficient of viscosity η in absolute (C.G.S.) units has been determined by different investigators, with the results given below:—

$\eta \times 10^7$.	*Temperature.*	*Observer.*
2203	14°·7	Schultze.[11]
2200	12°·0	Tänzler.[12]
2746	99° 6	
3231	183°·0	
2201	15°·5	Rankine.[13]
2102	0°·0	Rankine.[14]

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[1] Kuenen and Randall, *Proc. Roy. Soc.*, 1895, **59**, 60.

[2] Onnes and Crommelin, *Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 614, 1012; 1911, **14**, 158; 1912, **15**, 273, 952. Holborn and Schultze, *Ann. Physik*, 1915, [iv.], 10[illegible].

[3] Watson, *Trans. Chem. Soc.*, 1910, **97**, 833.

[4] Rayleigh and Ramsay, *Phil. Trans.*, 1895, **186**, 187.

[5] Estreicher, *Zeitsch. physikal. Chem.*, 1899, **31**, 176.

[6] Fox, *Trans. Faraday Soc.*, 1909, **5**, 68.

[7] Antropoff, *Proc. Roy. Soc.*, 1910, A, **83**, 474.

[8] Donnan, *Phil. Mag.*, 1900, [v.], **49**, 423.

[9] Kistiakowsky, *J. Russ. Chem. Soc.*, 1897, **29**, 291.

[10] Rayleigh, *Proc. Roy. Soc.*, 1896, **59**, 198.

[11] Schultze, *Ann. Phys.*, 1901, [iv.], **5**, 140.

[12] Tänzler, *Ber. deut. phys. Ges.*, 1906, **4**, 222.

[13] Rankine, *Proc. Roy. Soc.*, 1910, A, **83**, 265, 516.

[14] Rankine, *ibid.*, 1910, A, **84**, 181.

Rayleigh observed that the viscosity of argon increased with rise of temperature more rapidly than did that of the common diatomic gases,[1] and Rankine[2] showed that if this increase followed a linear law of the type

$$\eta_\theta = \eta_0 (1 + \beta\theta),$$

then β, the temperature coefficient of increase of viscosity of the gas, has the value 283×10^{-5}

The *refractivity* of argon has been determined by methods essentially similar to those described under Helium (p. 310): the principal results are tabulated below:—

Wave-Length (λ).	$(\mu - 1) \times 10^7$.	*Remarks.*	*Authority.*
White light	2808	Assuming value 2922 for air ($\lambda = 5894$).	Rayleigh.[3]
,,	2828		Ramsay and Travers[4]
6563	2829		Burton.[5]
5896	2837		,,
6439	2796		Ahrberg.[6]
5790 – 70	2803		,,
5461	2816		,,
4359	2851		,,
5461	2823		C. and M. Cuthbertson.[7]

Burton expressed his results by the formula

$$\mu = 1{\cdot}0002792 + \frac{1{\cdot}6 \times 10^{-14}}{\lambda^2}$$

(*cf.* Helium, p. 311), but C. and M. Cuthbertson give preference to a formula of the Sellmeier type,

$$\mu - 1 = \frac{C}{n_0^2 - n^2}.$$

At N.T.P. their values for the constants in this equation are given in the following table, together with those calculated from other results, for the sake of comparison:—

	$C \times 10^{-27}$.	$n_0^2 \times 10^{-27}$.
Burton	9 124	16335
Ahrberg . .	7 437	13516
C. and M. Cuthbertson	9·48264	17009

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[1] Rayleigh, *Proc. Roy. Soc.*, 1900, **66**, 68

[2] Rankine, *loc. cit.*

[3] Rayleigh, *Proc. Roy. Soc.*, 1896, **59**, 203.

[4] Ramsay and Travers, *ibid.*, 1897, **62**, 225; 1899, **64**, 190; 1901, **67**, 331.

[5] Burton, *ibid.*, 1908, **A**, **80**, 390.

[6] Ahrberg, *Inaugural Diss.*, Halle, 1909.

[7] C. and M. Cuthbertson, *Proc. Roy. Soc.*, 1910, **A**, **84**, 13.

Argon has a very low *dielectric cohesion* (38)—one-fifth that of air (205), and one-eleventh that of hydrogen (419).[1] In this respect it shows a resemblance to the monatomic vapour of mercury, the dielectric cohesion of which is 0·85 that of air—a very low figure considering the density of the gas.[2] The dielectric cohesion of argon is unaffected by change of pressure, but is markedly increased by admixture with other gases, whether diatomic gases like oxygen and nitrogen or the vapour of mercury.

The spark-gap (sparking distance) is about 40 per cent. greater in argon than in air, hydrogen, etc., under comparable conditions (*vide* Helium, p. 312).[3]

The lines seen in the spectrum of argon vary with the conditions.[4] If a discharge at 2000 volts be passed from a storage battery (or other similar source of continuous current) through the gas under reduced pressure, it emits a red glow; but when the discharge is oscillatory (*e.g.* with a spark-gap and condenser interposed) the colour of the light at once changes to blue. Proximity to a Herz oscillator will bring about a similar change in the character of the light, and a Geissler tube containing rarefied argon may, consequently, be used to detect electrical waves.[5] Stead has stated, as the result of investigations with a lime cathode, that the red spectrum is the spectrum of the positive column—even when produced under very low pressures—while the blue spectrum is that of the cathode beam.[6]

A very large number of lines in the spectrum have been measured, but only the more important of these are given in the following list. The reader desirous of further detail is referred to the original memoirs.[7]

"RED" SPECTRUM OF ARGON (Uncondensed Discharge).

Wave-Length.	*Intensity.*	*Wave-Length.*	*Intensity.*	*Wave-Length.*	*Intensity.*
7066·6	7	4272·30	8	4182·00	7
6964·8	8	4266·43	8	4164·30	7
5607·44	8	4259·49	9	4158·72	10
4510·85	7	4200·80	10	4014·56	8
4348·11	8	4198·16	10	3949·11	8
4345·32	7	{ 4191·84	10	3834·77	8
4333·71	8	{ 4190·81	7	3567·79	7
4300·25	8				

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[1] Bouty, *Compt. rend.*, 1904, 138, 616; 1907, 145, 225; *Ann. Chim. Phys.*, 1911, [viii.], 23, 5; 1913, [viii.], 28, 545.
[2] Bouty, *Compt. rend.*, 1904, 138, 1691, and *loc. cit.*
[3] See also, Ewers, *Ann. Physik*, 1905, [4], 17, 781.
[4] Friedlander, *Zeitsch. physikal. Chem.*, 1896, 19, 657.
[5] Trowbridge and Richards, *Amer. J. Sci.*, 1897, [iv.], 3, 15; *Phil. Mag.*, 1897, [v.], 43, 77.
[6] Stead, *Proc. Camb. Phil. Soc.*, 1912, 16, 607.
[7] Eder and Valenta, *Anzeiger K. Akad. Wiss. Wien*, 1895; *Sitzungsber. K. Akad. Wiss. Wien*, 1895; *Denkschr. K. Akad. Wiss. Wien*, 1896. Kayser, *Astrophys. J.*, 1896, 4, 1; *Sitzungsber. K. Akad. Wiss. Berlin*, 1896, p. 551. Crookes, *Phil. Trans.*, 1895, A, 186, 243; the red end of the red spectrum has been investigated by Runge, *Astrophys. J.*, 1899, 9, 281; Runge and Paschen, *ibid.*, 1898, 8, 99. These results are summarised in Watts's *Index of Spectra*, vol. F, p. 21, vol. H, p. 1, vol. M, p. 10. For the canal-ray spectrum of argon *see* Stark, Wendt, Kirschbaum, and Kunzer, *Ann. Physik*, 1913, [iv.], 42, 241.

"BLUE" SPECTRUM OF ARGON (Condensed Discharge).

Wave-Length.	*Intensity.*	*Wave-Length.*	*Intensity.*	*Wave-Length.*	*Intensity.*
5559·02	8	3781·02	7	3285·91	7
4880·00	8	3729·45	9	2942·94	7
4806·17	6	3638·02	7	2806·3	8
4609·74	7	3588·63	9	2769·7	8
4426·17	8	3582·55	7	2753·9	8
4348·22	9	3576·81	8	2744·9	8
4104·11	7	3561·21	7	2708·4	8
4014·00	7	3559·70	8	2647·6	8
3928·75	7	3546·01	7	2516·8	8
3868·72	7	3545·79	7	2515·6	8
3850·72	8	3491·72	9		

The Döppler effect has been observed for certain lines in the spectrum of argon.[1]

Argon is diamagnetic.[2]

The *thermal conductivity* of argon, $K = 0·00003894$ at 0° C.[3] When this value is substituted in the equation

$$K = f.\eta.c_v,$$

where η = the viscosity and c_v the specific heat of the gas at constant volume, we find (as in the case of helium, *q.v.*) that

$$f = 2·501.$$

This value approximates closely to that obtained theoretically by the development of Maxwell's theory, and therefore affords evidence for the simple nature of the argon molecule.[4]

Determinations of the thermal conductivity of argon at very low pressures gave peculiar results which are at present unexplained.[5]

Direct determination of the *specific heat* of argon at very high temperatures (1300°-2500° C.) have been made by exploding the gas with a known amount of electrolytic gas in a large spherical bomb provided with a special device for detecting and recording pressure variations. It was thus found that at constant volume the molecular specific heat is 2·977 cals.[6]

The specific heats at constant pressure and constant volume at ordinary temperatures have not been determined, but the ratio between these quantities has been found by the method of Kundt's tube (*vide* Helium, p. 316). A particular tube, which gave in air the value $\lambda/2 = 34·67$ mm., gave in argon $\lambda/2 = 31·68$ mm.; whence $\gamma = 1·65$.[7]

Liquefaction.—No difficulty is met with in the production of both liquid and solid argon, as the boiling-point and melting point lie between the boiling-point of freshly prepared liquid air and that of liquid air which has been kept.

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[1] Dorn, *Physikal. Zeitsch.*, 1907, **8**, 589. [2] Tänzler, *Ann. Physik*, 1907, [iv.], **24**, 936.

[3] Schwarze, *Ann. Physik*, 1903, [iv.], **11**, 303.

[4] *Cf.* Wachsmuth, *Physikal. Zeitsch.*, 1908, **9**, 235.

[5] Soddy and Berry, *Proc. Roy. Soc.*, 1910, **A**, **84**, 576.

[6] Pier, *Zeitsch. Elektrochem.*, 1909, **15**, 536.

[7] Rayleigh and Ramsay, *Phil. Trans.*, 1895, **186**, 187. See also Strieder, *Ber. deut. physikal. Ges.*, 1914, **16**, 615.

Liquid argon is colourless and transparent and boils at −186·1° C.;[1] at the boiling-point the density is 1·4046:[2] when cooled by external means or by its own evaporation, it solidifies to a white mass which crystallises in the regular system,[3] and melts at −187°·9 C., less than 3° below the boiling-point.

The critical constants of argon are as follows:—

Critical temperature[1]	−122°·44
Critical pressure[4]	47·996 atmos.
Critical density[5]	0·509 gm./cc.

The triple point of argon is −189°·3.[6] The vapour pressure of solid argon is 411 mm. at −190°·9: by addition of oxygen it is raised to 420 mm. at that temperature and then remains constant, in spite of continued addition of oxygen, as long as any solid argon remains. We are here dealing with a saturated solution of solid argon in liquid oxygen; it contains 92·7 per cent. of argon by volume, and the vapour in equilibrium with it contains 97·8 per cent. of argon.[7] The vapour pressures of liquid argon from the critical temperature to the triple point and of solid argon from the triple point to −206° C. have been determined, and from these data it has been calculated that the molecular heat of vaporisation of the liquid is 12·92 calories at −125°·49, 24·01 calories at −140°·80, and 35·00 calories at −183°·06.[6]

The equation for the rectilinear diameter for argon has been found to be $D_t = 0·20956 - 0·0026235t$ (temperature in degrees C.). The coefficient of *t*, *i.e.* the slope of the diameter, is greater than for any other gas except xenon.[8] The density of liquid argon varies from 1·4233 at 84° abs. to 1·3845 at 90° abs.[2]

In conclusion, it may be of interest to note that it has been recorded in one case[9] that argon exhibited "phosphorescent effects" during an experiment in which it was repeatedly passed over heated metallic calcium and copper oxide respectively. The phosphorescence is stated to have become more intense as the gas became purer. No attempt seems to have been made to explain this phenomenon; but there is at least a superficial resemblance to the observations recorded under Neon (p. 328), and the matter appears to be worth further investigation.

Chemical Inertness.—Argon is generally believed to be chemically inert, but it may be of interest to give an account, as was done in the case of helium, of the experimental evidence upon which this belief rests.

Argon is not acted upon by any of the agents—magnesium, calcium, lithium, calcium carbide, oxygen, potash, copper oxide, etc.—used in removing nitrogen and oxygen from air and in purifying the residual gas. This is evidenced by the fact that the proportion of argon in air determined by processes involving the use of these reagents agrees with that found by other methods. Moreover, it does not combine with titanium, boron, or uranium when heated in contact with these elements, or with fluorine at the ordinary temperature or under the influence of the electric spark.[1]

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[1] Ramsay and Travers, *Phil. Trans.*, 1901, A, **197**, 47; *cf.* Olzewski, *ibid.*, 1895, A, **186**, 253.

[2] Baly and Donnan, *Trans. Chem. Soc.*, 1902, **81**, 914.

[3] Wahl, *Proc. Roy. Soc.*, 1912, A, **87**, 371.

[4] Crommelin, *Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 54.

[5] Crommelin, *ibid.*, 1910, **13**, 607; *cf.* $T_\kappa = -117°·4$ C., $P_\kappa = 52·9$ atmos. (Ramsay and Travers, *Proc. Roy. Soc.*, 67, 329), $D_\kappa = 0·5149$ (Goldhammer, *Zeitsch. physikal. Chem.*, 1910, **71**, 577), also $D_\kappa = 0·530$ (Mathias, Onnes, and Crommelin, *vide infra*).

[6] Crommelin, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 477; 1914, **17**, 275. The triple-point pressure is 521·4 mm. (Holst and Hamburger, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 872.)

[7] Inglis, *Phil. Mag.*, 1906, [vi.], **11**, 640.

[8] Mathias, Onnes, and Crommelin, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 667, 960.

[9] Fischer and Hähnel, *Ber.*, 1910, **43**, 1435.

Rayleigh and Ramsay[2] attempted to cause argon to combine with the reagents enumerated below, but in no case was there any absorption of the gas :—

Hydrogen.
Chlorine.
Phosphorus.
Sulphur.
Tellurium.
Sodium.

Sodium hydroxide } (at red
Soda-lime } heat)
Potassium nitrate (fused).
Sodium peroxide.
Sodium persulphide.
Calcium persulphide.

Nitrohydrochloric acid.
Bromine water.
Potassium permanganate and hydrochloric acid.
Platinum black.

Other experiments have shown that argon is unaffected by a carbon arc maintained in the gas for several hours, or by the silent electric discharge in presence of the vapour of carbon tetrachloride.[3] By the action of producer gas (which of course contains argon) on a mixture of barium carbonate and carbon at the temperature of the electric arc, a product rich in barium cyanide is obtained, but when a sample of this material was completely decomposed according to Dumas' method the nitrogen recovered was found to contain no argon.[4] Similarly, it has been proved that argon has no action on magnesium, as the magnesium nitride obtained by heating the metal in air, on treatment with water yielded ammonia and a small amount (50 c.c. from 500 gm. nitride) of gas which was shown to contain no argon.[5] Argon does not pass through platinum, palladium, or iron at 900°-950°, under a pressure of 1 atmosphere, and therefore forms no compound or solid solution with these metals.[6] It has been shown independently that argon has no appreciable solubility in solid or liquid copper, silver, gold, nickel, iron, palladium, aluminium, magnesium, uranium, or tantalum.[7]

It has been suggested that this inertness might be purely a matter of temperature; and argon at ordinary temperatures has been compared with mercury vapour, which at 800° C. would appear to be incapable of combining with any other element.[8] This analogy is obviously imperfect, and argon should be compared rather with non-metals of low atomic weight and density than with mercury.[9]

It seemed likely that any compound of argon that might be produced would be endothermic, and, very possibly, unstable: if this were the case it might be possible to cause its formation at a high temperature and preserve it from decomposition by rapidly cooling it to a low temperature. Fischer, therefore, devised an apparatus in which an arc or spark discharge could be maintained between metallic electrodes submerged in liquid argon. Various metals were used—cadmium, titanium, tin, lead, antimony, and bismuth—and in some cases small amounts of metallic nitride were formed from traces of nitrogen present in the argon, but in no case was any evidence obtained of combination between the metal and argon.[1]

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[1] Moissan, *Compt. rend.*, 1895, **120**, 966.
[2] Rayleigh and Ramsay, *Phil. Trans.*, 1895, **186**, 187.
[3] Ramsay and Collie, *Proc. Roy. Soc.*, 1896, **60**, 53.
[4] Ramsay and Collie, *loc. cit.*
[5] Rayleigh and Ramsay, *Phil. Trans.*, 1895, **186**, 187; Crookes, *Chem. News*, 1895, **72**, 99; Ramsay, *ibid.*, 51; *Ber.*, 1898, **31**, 3111.
[6] Ramsay and Travers, *Proc. Roy. Soc.*, 1897, **61**, 267.
[7] Sieverts and Bergner, *Ber.*, 1912, **45**, 2576.
[8] Rayleigh and Ramsay, *loc. cit.*
[9] See Hill, *Amer. J. Sci.*, 1895, [iii], **50**, 359.

Such are the negative results hitherto obtained: it is, however, necessary to give a brief resumé of those cases which have been put forward as positive evidence of the formation or existence of compounds of argon.

It is a fact that if a powerful discharge be sent through argon in a vacuum tube having platinum or magnesium electrodes, the spectrum of the gas gradually diminishes in intensity and finally vanishes. This phenomenon at first received the obvious explanation—that the argon was absorbed or occluded by the electrodes;[2] but it is now known that the inert gases, when freed from ordinary diatomic gases by combination of the latter with the electrodes, may become fluorescent and even non-conducting at pressures measurable on a mercury barometer.[3] On the other hand, attention has been called by Ramsay[4] to the fact that electrodes of platinum, magnesium, aluminium, zinc, cadmium, antimony, and mercury always exhibit more "spluttering" in inert gases than in hydrogen, oxygen, nitrogen, etc.; and that vacuum tubes filled with inert gases that have been confined over mercury more frequently show the spectrum of mercury than do tubes similarly filled with ordinary gases.

Again, Cooke has stated that the vapour-density of zinc is 12 per cent. higher in argon than in nitrogen, and this has been put forward as evidence of a tendency to form a compound.[5] But it has since been shown that Cooke's results are untrustworthy, and the vapour densities of zinc, aluminium, and magnesium are unaffected by the presence of argon:[6] this argument therefore falls to the ground.

A very extensive series of experiments was made by Berthelot in order to ascertain the effect of the silent electric discharge on mixtures of argon with the vapours of volatile organic compounds—both fatty and aromatic—and of carbon disulphide, in presence of mercury vapour. With the aromatic compounds (but not with the aliphatic compounds) an absorption of argon was recorded in every case. The diminution in volume of the gas varied from 1 per cent. to 8 per cent. in various experiments, and was accompanied by a green luminosity the spectrum of which showed the lines of argon, mercury, carbon, and hydrogen.[7]

At one time it seemed probable that sufficient care had not been taken to ensure the removal of nitrogen from the gas, and that the phenomena observed were due to the presence of that gas;[8] but Ramsay has repeated these experiments, and has found that while both argon and nitrogen are present, the ordinary violet glow is observed, but when all nitrogen has been removed, the tube gives a brilliant green glow which shows the mercury spectrum.[1] The contemplation of these results has a very disquieting effect upon the mind accustomed to regard all these gases as invincibly indifferent to all other elements, and further experiment seems to be needed.

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[1] Fischer and Iliovici, *Ber.*, 1908, **41**, 3802 and 4449; 1909, **42**, 527; Fischer and Schröter, *Ber.*, 1910, **43**, 1442 and 1454.

[2] Troost and Ouvrard, *Compt. rend.*, 1895, **121**, 394; Friedlander, *Zeitsch. physikal. Chem.*, 1896, **19**, 657.

[3] Soddy, *Proc. Roy. Soc.*, 1907, **78**, 429.

[4] See note to paper by Cooke, *Proc. Roy. Soc.*, 1906, **A**, **77**, 149.

[5] Cooke, *Zeitsch. physikal. Chem.*, 1906, **55**, 537.

[6] Von Wartenberg, *Zeitsch. anorg. Chem.*, 1907, **56**, 320.

[7] Berthelot, *Compt. rend.*, 1895, **120**, 581, 1316, 1386; 1897, **124**, 113; 1899, **129**, 71, 133, 378.

[8] *Cf.* Dorn and Erdmann, *Annalen*, 1895, **287**, 230; Berthelot, *Compt. rend.*, 1897, **124**, 528.

Villard states that when pure argon is compressed at 150 atmospheres in the presence of water at 0°, local supercooling causes the formation of a solid, crystalline hydrate. The dissociation pressure of this body is given as 105 atmospheres at 0° and 210 atmospheres at 10°.[2]

Detection and Estimation.—The detection or estimation of argon in a mixture of gases is carried out by methods essentially the same as those used for its preparation. For example, in detecting the argon present in air, oxygen is absorbed by metallic copper, and nitrogen by heated lithium, calcium, or Maquenne's mixture, and the residual gas is examined spectroscopically. Fairly complete removal of nitrogen is necessary, as its spectrum readily masks that of argon: even 37 per cent. of argon in nitrogen can scarcely be detected spectroscopically.[3] To estimate the amount of argon present the same procedure is followed, except that special precautions are taken to prevent any leakage of gas, and the last traces of oxygen, nitrogen, and hydrogen are absorbed by red-hot metallic calcium. The method of using lithium as an absorbent for nitrogen, etc., has been elaborated and used more especially by Schloesing.[4]

The purity of argon may be tested by a determination of its dielectric cohesion: 1 per cent. of air or other diatomic gas multiplies it about 2½ times.[5]

Atomic Weight.—As argon forms no definite compounds its atomic weight cannot be determined in the usual manner; indeed, the usual chemical conception of the atom as the least part of an element which exists in the molecules of its compounds cannot be held in reference to argon or any other of the inert gases. The molecular weight is determined accurately from the density; and there is much evidence for the belief that the molecule is monatomic and that, therefore, the atomic weight is identical with the molecular weight.

Argon shows a close resemblance to the monatomic vapour of mercury in possessing a very low dielectric cohesion (see p. 339), and the value obtained for the thermal conductivity of the gas points to simplicity of molecular structure (see p. 340). What is usually regarded as the most conclusive evidence in this respect is obtained by the determination of the ratio of the specific heats at constant pressure and constant volume: the value 1·65, obtained for argon, is in agreement with that calculated from theoretical considerations[6] and found in the case of other gases which are almost certainly monatomic.[7] J. J. Thomson's method of analysis by positive rays points definitely to the same conclusion (p. 295).

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[1] See note, *loc. cit.*

[2] Villard, *Compt. rend.*, 1896, 123, 377.

[3] Collie and Ramsay, *Proc. Roy. Soc.*, 1896, 59, 257; Schmidt, *Ann. Physik*, 1904, [iv.], 14, 801.

[4] Schloesing, *loc. cit.*,

[5] Bouty, *Compt. rend.*, 1907, 145, 225.

[6] See this Vol., Part I., p. 97.

[7] See Helium, p. 323.

The work of Eotvos, Ramsay, and Shields has shown that for non associating liquids the value of the rate of change of the molecular surfac energy with the temperature is approximately constant (C.G.S. – 2·12 units) The surface tension of liquid argon has been determined by observation of it rise in a capillary tube,[1] and from these results the molecular weight o argon in the liquid state is calculated to be 15·9, a figure in sufficientl good agreement with the accepted value 39 9 (O = 16).

Lastly, there is the evidence of the general relationship of argon to th other inert gases and to the elements in the first and seventh groups of th periodic system. With one exception these relationships are in agreemen with the position in the system occupied by argon, if it is given the atomi weight 39·9. The exception is, of course, the anomaly that exists in the fac that argon, if it is to occupy a place among the elements of Group 0, mus precede potassium, the atomic weight of which is 39·1. This disturbing fac must not, however, be permitted to obscure our vision of the greater numbe of considerations which confirm the accepted atomic weight.

The International Atomic Weight Committee in 1911 adopted the valu 39·88, which is still (1917) to be found in their table. The density measurements made by Schultze in 1915 indicate that this figure is too low (see p. 337).

Application.—Argon is used for filling certain types of metal filamen electric lamps[2]

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[1] Walden, *Zeitsch. physikal. Chem.*, 1909, **65**, 129; Baly and Donnan, *Trans. Chem Soc.*, 1902, **81**, 914; Rudorf, *Ann. Physik*, 1909, [iv.], **20**, 751; Crommelin, *Proc. Chem Soc.*, 1914, **30**, 248.

[2] In this connection, for the analysis of argon-nitrogen mixtures, see Hamburger an Filippo, *Chem. Weekblad*, 1915, **12**, 2; *Zeitsch. angew. Chem.*, 1915, **28**, 75; Holst an Hamburger, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 872.

CHAPTER V.

KRYPTON (Kr).

History.—Krypton was discovered by Ramsay and Travers in the residues from the evaporation of a large quantity (30 litres) of liquid air used for the liquefaction and isolation of argon.[1] From these residues a gas was obtained which had a density of 22·5 (H = 1), which had the ratio of the specific heats, $C_p/C_v = 1·66$, and was therefore presumably monatomic, and, further, gave an entirely new spectrum. This gas was named *krypton* (κρυπτόν, the hidden one).

Further investigation of these heavy residues yielded yet another gas having a density of about 65 and a spectrum distinct from that of the other gases: it was named *xenon* (ξένος, the stranger).

Ladenburg and Krugel evaporated a larger quantity (850 litres) of liquid air, collected the least volatile residues, reliquefied this gas at the temperature of the liquid air, and fractionally evaporated the liquid. Their results confirmed the conclusion of Ramsay that two inert gases, denser than argon, existed in small amounts in air.[2]

Occurrence.—Krypton occurs in the atmosphere to the extent of about 1 part by volume in 20,000,000.[3] It has also been detected spectroscopically in the gases evolved from twenty-six mineral springs in France.[4] The amount present is 1·2 times that in air.[5]

Isolation.—Hitherto krypton has been obtained only from the atmosphere, and the methods that have been used for its isolation will now be described.

A mixture of krypton with xenon and traces of other gases may be obtained from liquid air by allowing the more volatile constituents to evaporate (*vide supra*). A better method consists in passing a stream of dry air free from carbon dioxide through a spiral tube filled with glass-wool and cooled in a bath of boiling liquid air. The pressure of the air passing through the apparatus is reduced below the vapour pressure of krypton at the temperature of the bath, and, under these conditions, impure krypton is deposited as liquid (or solid) in the tube, together with xenon and a little argon.[6]

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[1] Ramsay, *Ber.*, 1898, **31**, 3111; Ramsay and Travers, *Proc. Roy. Soc.*, 1898, **63**, 405.

[2] Ladenburg and Krugel, *Sitzungsber. K. Preuss. Akad.*, 1900, p. 727.

[3] Ramsay, *Proc. Roy. Soc.*, 1903, **71**, 421; 1908, **A**, **80**, 599.

[4] Moureu and Lepape, *Compt. rend.*, 1909, **149**, 1171; Moureu and Biquard, *Compt. rend.*, 1906, **143**, 795.

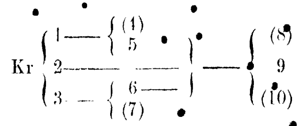
[5] Moureu and Lepape, *Compt. rend.*, 1911, **152**, 934.

[6] Dewar, *Proc. Roy. Soc.*, 1901, **68**, 362.

A rough separation of krypton from xenon may be effected by taking advantage of the difference between the vapour pressures of these substances at the temperature of liquid air (17 mm. and 0·17 mm. respectively). From the mixture of solid krypton and xenon a gas consisting chiefly of krypton, with small traces of argon, may be pumped off. Some krypton may be retained below the surface of the solidified xenon, but this can be removed by alternate vaporisation and solidification of the heavier gas.[1]

The cooled charcoal method (*cf.* p. 324) is also applicable to the isolation of fairly pure krypton and xenon. It is found that if "atmospheric" argon is subjected to the action of cocoanut charcoal cooled to a temperature of − 120° C., the whole of the krypton and xenon and some argon are absorbed. By placing the first charcoal bulb in connection with a second cooled in liquid air, nearly the whole of the argon can be removed. If the temperature of the first bulb be then allowed to rise to − 80° C., pure krypton is evolved, while at higher temperatures (up to 0° C.) a mixture of krypton and xenon is obtained. This mixture may be freed from krypton by condensing it in charcoal cooled to − 150° C. and then putting the first bulb in connection with a second cooled to − 180°: the krypton then passes over and condenses in the charcoal at the lower temperature, leaving the xenon in the first bulb. The two gases are then liberated separately from their respective bulbs by allowing them to warm up to the ordinary temperature.[2]

The crude krypton obtained by any of these methods must be purified further in order to fit it for the determination of physical constants. This can only be done by some process of fractionation, a good example of which is found in the work of Moore.[3] The residues from the evaporation of 120 tons of liquid air were first fractionated at the temperature of liquid air (*vide supra*), and the impure krypton thus obtained was condensed in a bulb cooled to − 130° C. in a bath of liquid air and light petroleum. This liquid was fractionally evaporated, and the three fractions obtained were further fractionated in the manner indicated in the following diagram:—



The fractions 4, 8, 7, and 10 were rejected as possibly containing argon or xenon, while fraction 9 was taken as pure krypton.

Properties.—Krypton is a colourless gas. It has not been stated definitely whether it has any odour or taste, and indeed it is possible that the experiment has never been tried. There is, however, no reason to suppose that it differs in this respect from the other members of the group.

The *density* of krypton was originally determined by Ramsay and Travers, but as they had at their disposal only 12 c.c. of gas, weighing about 0·045 gram, their result was, naturally, only approximate. The value of this constant was redetermined with great care by Moore, using fractions 8 and 9 of his gas obtained as described above. Fraction 9 was further refractionated ten times by Ramsay and Cameron, and the density of their final product determined. The value found in the mean was 41·506 (O = 16),[1] *i.e.* the weight of a normal litre of krypton is 3·708 grams.

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[1] Ramsay and Travers, *Proc. Roy. Soc.*, 1901, 67, 329; Liveing and Dewar, *ibid.*, 1901, 68, 389; Moore, *Trans. Chem. Soc.*, 1908, 93, 2181; *Proc. Roy. Soc.*, 1908, **A**, 81, 195.

[2] Valentiner and Schmidt, *Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 38, 816.

[3] Moore, *Trans. Chem. Soc.*, 1908, 93, 2181; *Proc. Roy. Soc.*, 1908, **A**, 81, 195.

The *compressibility* of krypton has been measured by Ramsay and Travers at considerable pressures (over 20 metres of mercury):[2] their results show that the value of *pv* decreases markedly with increase of pressure. From a critical discussion of the available data,[3] it seems probable that at 0° and between 0 and 1 atmospheres the compressibility coefficient of krypton is -0·00215.

Assuming the accuracy of this figure, and calculating according to the method of limiting densities, or calculating by Guye's method of critical constants for an easily liquefiable gas, we find for the molecular weight of krypton the value 82·92.

The *solubility* of krypton in water has been determined with two samples of the gas.[4] The mean result obtained for the absorption coefficient was 0·1249 at 0°, 0·0788 at 20°, and 0·0823 at 50°. If the solubility be plotted against temperature, the curve shows a distinct minimum solubility about 30°–40° C.

The *viscosity* of krypton has been determined by Rankine with the apparatus described under Helium (p. 309). At 10·6° C. it has a value 1·361 times that of air. Its value at 0° in absolute (C.G.S.) units is 2·334.[5] If the increase of viscosity with temperature follows a linear law of the type

$$\eta_\theta = \eta_0(1 + \beta\theta),$$

then

$$\beta \times 10^5 = 308.^6$$

The *refractivity* of krypton was first determined by the discoverers, who found it to be 1·449 times that of air.[7] Later determinations[8] have given the value $\mu - 1 = 428{\cdot}74 \times 10^{-6}$ at N.T.P. for the green mercury line ($\lambda = 5461$); and its dispersion at N.T.P. is given by

$$\mu - 1 = \frac{C}{n_0^2 - n^2},$$

where

$$C = 10{\cdot}6893 \times 10^{27}$$

and

$$n_0^2 = 12767{\cdot}9 \times 10^{27}.$$

The passage of an electrical discharge through a vacuum tube containing krypton causes the emission of light of a pale-violet colour.[9] It is found that the *spectrum* of this light is profoundly influenced by the nature of the discharge. That obtained with the direct discharge has few lines, the chief of which are in the yellow and blue, with a group in the green; that seen when a jar and spark-gap are used shows a large number of lines in the blue.

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[1] Moore, *Trans. Chem. Soc.*, 1908, **93**, 2181; *cf.* Watson, *ibid.*, 1910, **97**, 833.

[2] Ramsay and Travers, *Phil. Trans.*, 1901, **197**, 47; *Proc. Roy. Soc.*, 1901, **67**, 329.

[3] Watson, *loc. cit.*

[4] Antropoff, *Proc. Roy. Soc.*, 1910, **A**, **83**, 474.

[5] Rankine, *Proc. Roy. Soc.*, 1910, **A**, **83**, 516.

[6] Rankine, *ibid.*, 1910, **A**, **84**, 181.

[7] Ramsay and Travers, *Proc. Roy. Soc.*, 1901, **67**, 329.

[8] C. and M. Cuthbertson, *Proc. Roy. Soc.*, 1910, **A**, **84**, 13; *cf.* C. Cuthbertson and Metcalfe, *ibid.*, 1908, **A**, **80**, 411; C. and M. Cuthbertson, *ibid.*, 1908, **A**, **81**, 440.

[9] Ramsay and Travers, *Proc. Roy. Soc.*, 1901, **67**, 328.

A list of the principal lines in the visible part of these spectra is given below[1]:—

Accurate determinations of the wave-length of certain krypton lines, by comparison with the red cadmium line by an interference method, have been made.[2]

FIRST KRYPTON SPECTRUM. (Uncondensed discharge.)

Wave-Length.	*Intensity.*	*Wave-Length.*	*Intensity.*
5871·12	10	4454·12	10
5570·50*	10	4400·11	6
5562·45	6	4376·33	10
4671·40	10	4362·83	9
4624·48	10	4319·76	10
4502·56	9	4318·74	8
4501·13	7	4274·15	10
4463·88	10		

* Probably the green *auroral* line.

OND KRYPTON SPECTRUM. (Condensed discharge.)

Wave-Length.	*Intensity.*	*Wave-Length.*	*Intensity.*
5633·17	6	4109·38	6
4765·90	6	4098·89	7
4762·60	5	4088·48	8
4739·16	7	4067·53	5
4659·04	5	4065·22	8
4634·05	5	4057·17	8
4619·31	6	4050·62	5
4615·46	5	4044·80	5
4577·40	6	3998·10	5
4523·32	5	3994·98	6
4475·18	7	3954·90	5
4355·67	10	3920·29	8
4317·98	5	3917·76	6
4300·67	5	3912·49	5
4293·10	6	3906·37	8
4145·28	6		

In this connection it is of interest to note that the spectrum of the *aurora borealis* contains a number of strong lines, all of which coincide exactly with prominent lines in the spectrum of krypton.[3] In particular this is true of the line $\lambda = 5570$, which is known to persist in the spectrum of krypton at pressures as low as $\frac{1}{23 \times 10^6}$ atmosphere. The pressure of the atmosphere is of this order of magnitude at a height of 80 miles, a height within the limits (50–125 miles) at which the aurora has been observed. It is hardly possible, then, to avoid the conclusion that the northern lights are due, in part at least, to the presence of krypton in the atmosphere.[1] The measurement of the intensity of the lines of the krypton spectrum has been used to estimate the proportion present in various spring gases.[2] The *Zeeman effect* in krypton has been investigated by Lohmann.[3]

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[1] See Baly, *Proc. Roy. Soc.*, 1903, 72, 84; *Phil. Trans.*, 1903, A. **202**, 183; *cf.* Liveing and Dewar, *Proc. Roy. Soc.*, 1901, 68, 360.

[2] Buisson and Fabry, *Compt. rend.*, 1913, 156, 945.

[3] Liveing and Dewar, *Proc. Roy. Soc.*, 1901, 67, 467.

Krypton is easily *liquefied* at temperatures above that of boiling liquid air: it boils at − 151°·7 C. The vapour-pressure ratio is 0·0167 (p. 294, footnote). The density of the liquid at its boiling-point is 2·155 grams per c.c., whence the molecular volume = 37·81.[4]

The critical temperature of the liquid is − 62°·5 C., and its critical pressure is 54·3 atmospheres.[4]

Krypton may be easily solidified by cooling in liquid air: it melts at − 169°.[5]

The *specific heat* of krypton has not been determined, and formerly the only data available as to the ratio of the specific heats were obtained with mixtures of krypton with other inert gases. This ratio has now been determined with a sample of pure krypton; the method used was that described under Helium (p. 316), and the following are the data obtained with air and krypton examined successively in the same tube:—

	Temperature.	*Half Wave-Length.*	*Density.*
Air . . .	19°	27·92	14·48
Krypton . .	19°	18·13	41·46

Hence for krypton the ratio C_p/C_v = 1·689.[6]

Atomic Weight.—It is believed that krypton has a monatomic molecule and that the atomic weight is, consequently, identical with the molecular weight and = 82·92 (p. 345). The reasons for this belief may be summarised briefly as follows:—

(1) The ratio of the specific heats at constant pressure and constant volume approximates closely to 1·667.

(2) The general properties of the gas indicate that it should occupy a position in the periodic classification of the elements between bromine (at.wt. = 80) and rubidium (at.wt. = 85·5), a position with which the atomic weight given above is in agreement.

(3) The positive ray method of analysis indicates that the gas is monatomic.

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[1] See Baly, *loc. cit.*; Page, *Proc. Phys. Soc.*, 1912, **24**, 138.

[2] Moureu and Lepape, *Compt. rend.*, 1911, **152**, 691.

[3] Lohmann, *Zeit. wiss. Photochem.*, 1908, **6**, 1, 41.

[4] Ramsay and Travers, *Proc. Roy. Soc.*, 1901, **67**, 329; *Phil. Trans.*, 1901, **197**, 47.

[5] Ramsay and Travers, *loc. cit.*; *cf.* Moore, *loc. cit.*; Ladenburg and Krügel, *Sitzungsber. K. Preuss. Akad. Wiss.*, 1900, p. 212.

[6] Ramsay, *Proc. Roy. Soc.*, 1912, **A**, **86**, 100.

CHAPTER VI.

XENON (X).

History.—Xenon was the last gas to be discovered by Ramsay and Traver in the least volatile residues of liquid air. A brief account of the manner o its discovery has been given under Krypton (p. 346), and the reader desirou of more detailed information is referred to the original memoir.[1]

Occurrence.—Xenon is present in the atmosphere to the extent o 1 vol. in 170,000,000 vols.; and is thus the least abundant of the inert gases Nevertheless, the atmosphere is the only available source of xenon. In view of the considerable solubility of xenon in water one would naturally expec that it would be dissolved by the rain and would ultimately find its way int spring- and river-waters; it has now been shown that xenon does exist in th gases evolved from many mineral springs.[2]

Isolation.—Hitherto xenon has usually been obtained along wit krypton in the heavy residues from the evaporation of large quantities o liquid air. The mixture is fractionated according to methods described unde Krypton (p. 346), and the heaviest and most easily condensed fractions ar fairly pure xenon.

Xenon may also be obtained from pure dry air, free from carbon dioxid and moisture, by the simple plan of passing it, under suitable reduce pressure, through a spiral tube filled with glass-wool immersed in a bath o liquid air. If the conditions are carefully regulated it is possible to obtain the greater part of the xenon present in the air condensed as a solid in th lass-wool.[3]

Xenon is more easily purified than krypton as it is always accumulated in the end fractions. Moreover, the vapour pressure of the solid at the tempera ture of liquid air is so small (0·17 mm.) that all other gases may be pumpe ff from it. It is usually found that while the greater part of the mor volatile gases may be removed in one operation, a small portion is occlude y the solid xenon. If, however, the solid be allowed to warm up and the gain cooled, the occluded gas is liberated and can be pumped off.

Properties.—Xenon is a colourless gas. Whether it has any taste, o dour is not known (*cf.* Krypton, p. 347).

The early determinations of its *density* were made by Ramsay and Travers,[4] but their result was necessarily of a provisional nature as they had only 3 c.c. of the gas. A subsequent determination is that of Moore, who, during an investigation of the residues from the evaporation of 120 tons of liquid air, obtained xenon in quantity sufficient for its thorough fractionation and exact weighing. These residues were freed from krypton and other gases at the temperature of liquid air (*vide supra*), and the impure xenon thus obtained was fractionated at − 130° C. The mean of two determinations made on the purest fraction gave for the density the value 65·35 (O = 16),[1] *i.e.* a normal litre of xenon weighs 5·851 grams.

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[1] Ramsay and Travers, *Phil. Trans.*, 1901, 197, 47; see also Moore, *Chem. News*, 1911, 03, 242.

[2] Moureu and Lepape, *Compt. rend.*, 1909, 149, 1171.

[3] Dewar, *Proc. Roy. Soc.*, 1901, 68, 360.

[4] Ramsay and Travers, *Phil. Trans.*, 1901, 197, 47.

The *compressibility* of xenon was investigated by Ramsay and Travers (*loc. cit.*), who found that the value of $p\,v$ decreased very markedly as the pressure increased. This behaviour is, of course, quite in accordance with the fact that the critical temperature of xenon is about the ordinary temperature, at which the experiments were conducted. Calculating according to Guye's method of critical constants, we have for the molecular weight of xenon the value 130·22.[2] From this result it can be calculated indirectly that at 0° and between 0 and 1 atmosphere the compressibility coefficient is equal to + 0·00690.

Xenon is relatively very soluble in water, its *absorption coefficient* being 0·2189 at 0° C. and 0·0878 at 50° C.: a point of minimum solubility occurring at about 40° C.[3]

The *viscosity* of xenon at 0° C. is $\eta_0 = 2{\cdot}107 \times 10^{-4}$ and if its variation with temperature is given by the linear equation:

$$\eta_\theta = \eta_0 (1 + \beta\theta),$$

then[4]

$$\beta = 3{\cdot}39 \times 10^{-3}.$$

The *refractivity* of the gas for white light was originally found to be 2·364 times that of air.[5] Later determinations have given the value $\mu - 1 = 705{\cdot}49 \times 10^{-6}$ for the green mercury line ($\lambda = 5461$). The dispersion at N.T.P. is given by the equations:

$$\mu - 1 = 0{\cdot}0006823\left(\frac{10{\cdot}14}{1 + \lambda^2 \times 10''}\right),$$

or

$$\mu - 1 = \frac{C}{n_0{}^2 - n^2},$$

where $C \times 10^{-27} = 1262418$, $n_0{}^2 \times 10^{-27} = 8977{\cdot}87$, and n is the frequency of the light.[6]

The passage of an uncondensed discharge through a vacuum tube containing xenon causes the emission of light of a sky-blue colour;[7] if a spark-gap and Leyden jar be interposed in the circuit the colour of the light changes to green. This change is similar in character to that seen under similar conditions in helium and krypton; and xenon, like these gases, has two spectra. A list of the more prominent lines of xenon is given below[8]:—

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[1] Moore, *Trans. Chem. Soc.*, 1908, 93, 2181; Watson, *ibid.*, 1910, 97, 833.

[2] Watson, *Trans. Chem. Soc.*, 1910, 97, 833.

[3] Antropoff, *Proc. Roy. Soc.*, 1910, A, 83, 474.

[4] Rankine, *Proc. Roy. Soc.*, 1910, A, 84, 181.

[5] Ramsay and Travers, *loc. cit.*

[6] C. and M. Cuthbertson, *Proc. Roy. Soc.*, 1908, A, 81, 440; 1910, A, 84, 13.

[7] Ramsay and Travers, *Proc. Roy. Soc.*, 1901, 67, 329.

[8] Baly, *Phil. Trans.*, 1903, A, 202, 183; see also Liveing and Dewar, *Proc. Roy. Soc.*, 1901, 68, 360.

FIRST XENON SPECTRUM. (Uncondensed Discharge.)

Wave-Length.	*Intensity.*	*Wave-Length.*	*Intensity.*	*Wave-Length.*	*Intensity.*
4923·28	6	4624·46	15	4116·15	7
4916·63	6	4582·89	5	4109·84	5
4807·19	6	4524·83	6	4078·94	10
4734·30	8	4501·13	10	3967 74	10
4697·17	7	4193·70	8	3951·16	10
4671·42	10				

SECOND XENON SPECTRUM. (Condensed discharge.)

Wave-Length.	*Intensity.*	*Wave-Length.*	*Intensity.*	*Wave-Length.*	*Intensity.*
6097·80	7	4921·68	6	4415·00	7
6051·36	7	4890·24	5	4406·99	5
6036·40	6	4887·47	5	4395·91	10
5976·67	7	4883 68	6	4393·34	10
5751·28	5	4876·68	7	4330·63	15
5727·15	5	4862·69	8	4296·52	5
5719·83	6	4844·50	10	4245·54	10
5667·85	6	4823·47	6	4238·37	10
5659·67	5	4698·20	5	4223·14	5
5616·99	6	4683·76	5	4215·77	5
5531·33	7	4652·15	6	4214·17	5
5472·90	7	4615·72	5	4213 80	5
5460·63	6	4603·21	10	4208·61	6
5450·71	5	4592·22	6	4193·25	8
5439·19	8	4585·64	10	4180·20	10
5419·40	10	4577 36	6	4158·14	5
5372·62	8	4545·34	8	4145·85	5
5339·56	9	4541·03	8	4109·20	6
5314·15	8	4532·67	5	4057·55	5
5292·40	10	4524·38	5	4050·19	6
5262·10	5	4481·01	7	3992·98	5
5260·65	5	4462·38	20	3950·70	8
5191·60	5	4418·28	10	3922 67	10
5080 88	7	4434·35	6	3908·00	7

The *Zeeman* effect in xenon has been studied by Lohmann.[1]

The ratio of the specific heats of xenon has been determined by Ramsay according to Kundt's method. The following data were obtained :-

	Tempera-ture.	*Half Wave-length.*	*Density.*
Air	19°	27·92	14·48
Xenon . . .	19°	14·32	65·11

Hence the ratio $C_p/C_v = 1·666$.[2]

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[1] Lohmann, *Physikal. Zeitsch.*, 1906, 7, 809.

[2] Ramsay, *Proc. Roy. Soc.*, 1912, A, 86, 100.

The *critical temperature* of xenon is +16·6° C., and the gas may be liquefied at this temperature by a pressure of 58·2 atmospheres.[1] The liquid is colourless and boils at −109·1° C. under atmospheric pressure.[2] Its density at the boiling-point is 3·06, whence the molecular volume = 42·7. Its vapour-pressure ratio (p. 294, footnote), is 0·0675. Xenon is easily solidified at the temperature of liquid air: its melting-point is about −140° C.[2]

The "rectilinear diameter" for xenon is given by the equation $D_t = 1·206 - 0·003055t$ (D_t = mean density of liquid and saturated vapour at t° C.) and the value of the coefficient of t, *i.e.* the slope of the diameter is greater than for any other gas. The density of the liquid varies from 1·468 at 16° to 1·987 at 0° and 2·694 at −59·3°.[3]

Atomic Weight.—No compounds of the element are known, and it is therefore impossible to apply to xenon any of the ordinary methods for the determination of atomic weight. It is, however, believed, for reasons exactly similar to those given under Krypton (p. 350), that the molecule of the gas is monatomic, and its atomic weight is taken as 130·2 (O = 16).

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[1] Patterson, Cripps and Whytlaw Gray, *Proc. Roy. Soc.*, 1912, **A**, **86**, 579.

[2] Ramsay and Travers, *Phil. Trans.*, 1901, **A**, **197**, 71.

[3] Patterson, Cripps and Whytlaw Gray, *loc. cit.*

CHAPTER VII.

NITON (Nt).

History.—The name *niton* was given by Gray and Ramsay to radium emanation.[1] Its history is, naturally, closely involved with that of radium (see Radium, Vol. III.), but it may be mentioned here that its discovery was due to Dorn.[2] It was early recognised that this product of the radioactive disintegration of radium was a gas, and resembled the inert gases in its indifference to platinum- and palladium-black, lead chromate, zinc and magnesium powder, and magnesium and lime at a red heat, to phosphorus burning in oxygen, and to sparking with oxygen.[3]

When, by the remarkable experiments mentioned later (p. 357), its density was determined and the molecular weight thereby found to be about 223, it became evident that, were it a monatomic gas, it would find a place in the periodic classification in the group of inert gases and in the same series as radium. It has since been found that its other physical properties accord well with those to be expected in an inert gas of atomic weight 223 (see Table I., p. 294), and niton is now, by general consent, given a place in Group 0.

Occurrence.—Niton doubtless occurs in all radium minerals; but as it undergoes radioactive change and only a minute amount can be present in equilibrium with the small quantity of radium, it is hardly surprising that it has not hitherto been detected.

It is undoubtedly the case that some radioactive substance is present in the atmosphere, because a negatively charged wire exposed to air acquires a radioactive deposit which can be removed thence by solution in ammonia, or by rubbing.[4] Observations on the rate of decay of this deposit indicate that it is due to the presence in the atmosphere, of the emanations of thorium and radium derived from thorium and radium contained in the soil.[5] The relative proportions of niton and thorium emanation present in the lower levels of the atmosphere appear to be very variable,[6] and it has been found that at

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[1] It was at one time proposed to call this substance *exradio*; Ramsay and Collie, *Proc. Roy. Soc.*, 1904, 73, 470.

[2] Dorn, *Naturforsch. Ges. für Halle a. S.*, 1900.

[3] Rutherford and Soddy, *Phil. Mag.*, 1902, [vi.], 4, 580; Ramsay and Soddy, *Proc. Roy. Soc.*, 1903, 72, 204.

[4] Elster and Geitel, *Physikal. Zeitsch.*, 1901, 2, 590; Rutherford and Allan, *Phil. Mag.*, 1902, [vi.], 4, 704; Allan, *ibid.*, 1904, [vi.], 7, 140.

[5] Simpson, *Phil. Trans.*, 1905, 205, A, 61; Gockel and Wulf, *Physikal. Zeitsch.*, [illegible]; Satterly, *Proc. Camb. Phil. Soc.*, 1912, 16, 514.

[6] [illegible], *Physikal. Zeitsch.*, 1908, 9, 295; Wilson, *Phil. Mag.*, 1909, [vi.], 17, [illegible]; [illegible], *Le Radium*, 1908, 5, 102; Harvey, *Physikal. Zeitsch.*, 1909, 10, 46.

Sestola, in the Apennines, at a height of 3000 feet, the proportion of the total atmospheric activity due to thorium varies from 29–73 per cent.[1] In general it may be said that thorium emanation preponderates in the lower levels of the atmosphere and niton in the higher levels.

The amount of niton present per cubic metre of air is approximately that which would be in equilibrium with $1\cdot0 \times 10^{-10}$ gm. of radium.[2]

Isolation.—Niton is continuously formed by the radioactive change of radium and its salts under all conditions. Solid radium salts always retain the whole of the niton—presumably in a state of solid solution,—but the greater part of the gas may be driven out by heating to about 800°. The proportion retained decreases as the temperature is raised and is independent of the duration of heating, but varies much with different preparations.[3] The niton may be pumped away directly, but the amount usually handled is so minute that it is necessary to wash it out with another gas, *e.g.* oxygen.

When an aqueous solution of a radium salt is kept in a closed flask niton is evolved, together with oxygen and hydrogen produced by the decomposition of the water. The amount of niton increases rapidly during the first few days and afterwards more slowly until, after about a month, the maximum amount which can be in equilibrium with the radium present is reached.

The hydrogen produced is about 5–10 per cent. in excess of that equivalent to the oxygen present: this is probably due to the action of the penetrating rays of radium, which bring about the conversion of water into hydrogen peroxide and hydrogen.[4] On exploding the gas, all the oxygen and most of the hydrogen are converted into water. If the residual gas be passed through a copper or glass spiral cooled in liquid air, the whole of the niton is condensed, and the residual hydrogen, together with any helium produced by the decomposition of the niton during the time it has been in the flask, may be pumped off.[5] A similar method may be used to condense niton from air.[6] The gas thus prepared usually contains a small amount of carbon dioxide produced by the oxidation of adventitious organic matter, but this can be removed by prolonged contact with baryta.

The amount of niton which can be obtained from radium is very small, as will be readily realised from the fact that the maximum amount that can be in equilibrium with 1 gram of radium is 0·585 cubic mm. at N.T.P.[7] Special methods have to be adopted in manipulating such minute quantities of gas, but space does not permit of their description here: the reader who is specially interested is referred to the original memoirs.

Properties.—Niton is a gas. This can be said with certainty, as it can be manipulated as a gas by means of a Töpler pump, can be seen to flow in the manner of a gas through the glass tubes of the apparatus,[3] obeys Boyle's law,[2] and can be liquefied and solidified by cooling.[8] It is colourless by transmitted light.

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[1] Pacini, *Physikal. Zeitsch.*, 1910, 11, 227.

[2] Ashman, *Amer. J. Sci.*, 1908, [vi.], 26, 119; Eve, *Phil. Mag.*, 1907, [vi.], 14, 724; see also Eve, *ibid.*, 1908, [vi.], 16, 622; Satterley, *ibid.*, 1908, [vi.], 16, 584; 1910, [vi.], 20, 1.

[3] Kolowrat, *Le Radium*, 1909, 6, 321; 7, 266.

[4] Debierne, *Compt. rend.*, 1909, 148, 703; *Le Radium*, 1909, 6, 65; Kernbaum, *Compt. rend.*, 1909, 148, 705; 149, 116 and 273; *Le Radium*, 1909, 6, 225.

[5] Ramsay and Collie, *Proc. Roy. Soc.*, 1904, 73, 470.

[6] Ashman, *loc. cit.*

[7] Rutherford, *Phil. Mag.*, 1908, [vi.], 16, 300; Rutherford and Boltwood, *Mem. Manchester Phil. Soc.*, 1909, 54, No. VI.; Rutherford and Geiger, *Proc. Roy. Soc.*, 1908, A, 81, 162 (calculated value); Gray and Ramsay, *Trans. Chem. Soc.*, 1909, 95, 1073; Debierne, *Compt. rend.*, 1909, 148, 1264; *Ann. Physique*, 1915, [ix.], 3, 18.

The *density* of the gas has been determined by direct weighing on a microbalance sensitive to 2×10^{-6} milligram, with a weight of niton of the order of $\frac{1}{1400}$ mgm.: the mean of several experiments gave the value 111·5 (H = 1).[4] This figure is in general agreement with the results of the effusion experiments of Debierne[5] and Perkins,[6] which gave the values 110 and 117·5 respectively.[7]

As radium (atomic weight = 226·0)[8] is transformed into niton with the loss of one α-particle, and as the α-particle is believed, on excellent grounds, to be identical with the atom of helium, it is to be expected that the atomic weight of niton would be 226·0 - 4·0 = 222·0. This figure agrees well with the molecular weight calculated from the density determinations quoted above, the one adopted by the International Commission is 222·4.

Niton is soluble in water: its absorption coefficient is approximately 0·5 at 0°, 0·3 at 15°, 0·27 at 18°,[9] 0·23 at 20°,[1] and 0·15 at 40°,[10] and thus has a large temperature coefficient. Above 75° C. the value of the absorption coefficient becomes very nearly constant and approximately equal to 0·11.[11] It is much more soluble in organic liquids, except glycerine, as the following values of the absorption coefficient at 15° C. indicate:—

Ethyl alcohol	7·2	Amyl alcohol	
Petroleum	9·5	Aniline	
Toluene	11·7	Carbon disulphide	
Glycerine	0·21		

It is less soluble in salt solution than in pure water, and Henry's Law is followed exactly in every case.[12]

When subjected to an electrical discharge, niton gives a distinct *spectrum*, which is the same whether the discharge is direct or oscillatory, and appears to be of the same character as the spectra of the other inert gases.[13] There is, however, some evidence that the relative intensity of the lines may vary with the pressure. The niton spectrum disappears after the discharge has been passed for three to five minutes, giving place first to the primary, and later to the secondary spectrum of hydrogen. The source of this hydrogen is not definitely known, but it is very probably occluded n the electrodes. The niton appears to be driven to the walls of the vacuum tube, and can be partially liberated again by prolonged heating.[1]

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[1] Ramsay and Soddy, *Proc. Roy. Soc.*, 1903, **72**, 204.

[2] Ramsay and Cameron, *Trans. Chem. Soc.*, 1907, **91**, 1266.

[3] Rutherford and Soddy, *Phil. Mag.*, 1903, [vi.], **5**, 561.

[4] Gray and Ramsay, *Proc. Roy. Soc.*, 1911, A, **84**, 536; also in *Ann. Chim. Phys.*, 1910, [viii.], **21**, 145, 574. For details of this extremely interesting work the reader is referred to the original memoir.

[5] Debierne, *Compt. rend.*, 1910, **150**, 1740.

[6] Perkins, *Amer. J. Sci.*, 1908, [iv.], **25**, 461.

[7] See also Makower, *Phil. Mag.*, 1905, [vi.], **9**, 56.

[8] Hönigschmid, *Monatsh.*, 1912, **33**, 253; 1913, **34**, 283.

[9] Kofler, *Phil. Mag.*, 1908, **9**, 6.

[10] R. Hofmann, *Physikal. Zeitsch.*, 1905, **6**, 337.

[11] Kofler, *Monatsh.*, 1913, **34**, 389.

[12] Ramstedt, *Le Radium*, 1911, **8**, 253; Boyle, *Phil. Mag.*, 1911, [vi.], [illegible]

[13] Cameron and Ramsay, *Proc. Roy. Soc.*, 1908, A, **81**, 210; Royds, *Phil. Mag.*, 1909, [vi.], **17**, 200; Watson, *Proc. Roy. Soc.*, 1909, A, **83**, 50.

The first measurements were made visually by Ramsay and Collie,[2] who observed that a very strong and persistent line, λ = 5596, coincided with a strong line seen by Pickering[3] in the spectrum of lightning. Since then numerous attempts have been made to map the spectrum by visual and photographic methods.[4] Their results are summarised and supplemented with new data in a paper by Watson,[5] which should be consulted for further information on this point.

Nothing is known as to the ratio of the specific heats of niton, but the monatomicity of its molecule is to be inferred from the agreement between the atomic weight calculated on theoretical grounds and the molecular weight deduced from its gaseous density, and from the fact that the volume of the gas obtained from a given weight of radium agrees with that calculated on the assumption that the molecule of niton is monatomic.

The minute amount of emanation usually obtained is found to condense and volatilise sharply between − 152° and − 154°, but with larger amounts it has been found possible to determine its vapour pressure at various temperatures.

Its critical temperature is 104° 5, and its critical pressure is 62·5 atmospheres. It boils at − 62° and freezes at − 71°, and its vapour pressure at the latter temperature is 500 mm. When examined under the microscope, the liquid is seen to be colourless and transparent; its density is about 5.[6] The solid is opaque, but its colour cannot be seen on account of its intrinsic luminosity.[7]

Niton is absorbed by cocoanut charcoal at the ordinary temperature, and is again evolved at higher temperatures, and this fact may be utilised in its purification.[8]

Radioactive Change of Niton.—The property of intrinsic luminosity is characteristic of niton in all states of aggregation, and is one evidence of the energy changes which accompany its disintegration. The intensity of the phosphorescence is greatest in the solid—possibly because of the lesser volume occupied—but both the gas and the liquid glow strongly. The colour of the light emitted by the solid varies from steel-blue at the melting-point to orange-red at lower temperatures.[9] Heat is also given out during the disintegration of the emanation.[10]

The continuous emission of energy is also shown by the slow decomposition of carbon dioxide, carbon monoxide, ammonia, hydrochloric acid, and

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[1] Rutherford, *Phil. Mag.* 1908. [vi.], 16, 300.

[2] Ramsay and Collie, *Proc. Roy. Soc.*, 1904, 73, 470.

[3] Pickering, *Astrophys. J.*, 1901, 14, 368.

[4] Ramsay and Cameron, *Proc. Roy. Soc*, 1908, A, 81, 210; Rutherford and Royds, *Phil. Mag.*, 1908, [vi.], 16, 313; Royds, *Phil. Mag.*, 1909, [vi.], 17, 202; *Proc. Roy. Soc.*, 1909, A, 82, 22.

[5] Watson, *Proc. Roy. Soc.*, 1909, A, 83, 50.

[6] Rutherford, *Phil. Mag.*, 1909, [vi.], 17, 723.

[7] Rutherford and Soddy, *Phil. Mag.*, 1903, [iv.], 5, 561; Rutherford, *ibid.*, 1909, [vi.], 17, 723; Gray and Ramsay, *Trans. Chem. Soc.*, 1909, 95, 1073; Laborde, *Compt. rend.*, 1909, 148, 1591.

[8] Satterley, Eve, p. 356; Satterley, *Phil. Mag.*, 1910, [vi.], 20, 778.

[9] Gray and Ramsay, *Trans. Chem. Soc.*, 1909, 95, 1073; Rutherford, *Phil. Mag.*, 1909, [vi.], 17, 723.

[10] Rutherford and Barnes, *Phil. Mag.*, 1904, [vi.], 7, 202.

It has also been stated that when solutions or compounds of the elements of the carbon group (silicon, titanium, zirconium, thorium, and lead) are subjected to the action of niton, carbon dioxide is always produced. This suggests a possibility that there may be a breaking-down of the molecules of these elements with formation of carbon, the lowest member of the series.[2] Niton will cause the oxidation of wet mercury, and turns ordinary white glass violet.[3]

It was at one time supposed that a change of copper into lithium and of water into neon had been observed,[4] but the validity of these observations is seriously open to question.[5]

For one or two days after its isolation niton undergoes a slow contraction to about one-half its original volume;[6] afterwards it slowly expands to about 3 to 3½ times the original volume.[7] This change corresponds to a change in the spectrum, that of niton disappearing completely after 3–4 days, and giving place to that of helium.[8]

The cause of the contraction is obscure, but it has been observed in every sample hitherto prepared, and is, perhaps, due to impurities. The slow expansion which takes place afterwards may be satisfactorily explained on the hypothesis that the α-particles given out during the radioactive change of the niton have such a high velocity that they are forced into the walls of the containing vessel and are only evolved again quite slowly. It has been found that if niton is confined in a glass tube the walls of which have a thickness less than the range of its α-particles in glass, an accumulation of helium can be observed in the outer space. This supports the preceding explanation of the slow increase in volume, and further proves conclusively the identity of the helium atom with the α-particle.[9] The period of half-change of niton is 3·75 days.[10]

It may be mentioned here that the evolution of helium from radium was first proved by Ramsay and Soddy,[11] and confirmed by Himstedt and Meyer:[12] the statement that the radioactive elements are elements undergoing decomposition was first made by Geoffrey Martin.[13] Assuming that 5 α-particles are expelled during the complete disintegration of one atom of radium, the volume of helium produced per day from 1 gram of radium

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[1] Ramsay, *Trans. Chem. Soc.*, 1907, 91, 931; Cameron and Ramsay, *ibid.*, 1907, 91, 1593; 1908, 93, 966 and 992; Perman, *ibid.*, 1908, 93, 1775; Usher, *ibid.*, 1910, 97, 389; Rutherford and Royds, *Phil. Mag.*, 1908, [vi.], 16, 812; Mme Curie and Mlle Gleditsch, *Compt. rend.*, 1908, 147, 345.

[2] Ramsay and Usher, *Ber.* 1909, 42, 2930; *cf.* Herschfinkel, *Compt. rend.*, 1911, 153, 255; *Le Radium*, 1911, 8, 417; Ramsay, *Compt. rend.*, 1911, 153, 373.

[3] Ramsay and Soddy, *Proc. Roy. Soc.*, 1903, 72, 204.

[4] Ramsay and Cameron, *Trans. Chem. Soc.*, 1907, 91, 1604; 1908, 93, 992.

[5] Rutherford and Royds, *Phil. Mag.*, 1908, [vi.], 16, 812; Mme Curie and Mlle Gleditsch, *Compt. rend.*, 1908, 147, 345; Perman, *Trans. Chem. Soc.*, 1908, 93, 1775. See also this series, Vol. II.

[6] Rutherford, *Phil. Mag.*, 1908, [vi.], 16, 300; Ramsay and Cameron, *Trans. Chem. Soc.*, 1907, 91, 1266.

[7] Dewar and Curie, *Compt. rend.*, 1904, 138, 190; Indrikson, *Physikal. Zeitsch.*, 1904, 5, 214; Himstedt and Meyer, *Ann. Physik*, 1904, [iv.], 15, 184.

[8] Ramsay and Soddy, *Proc. Roy. Soc.*, 1903, 72, 207.

[9] Rutherford and Royds, *Phil. Mag.*, 1909, [vi.], 17, 281.

[10] Rutherford and Soddy; Rumelin, *Phil. Mag.*, 1907, [vi.] 14, 550.

[11] Ramsay and Soddy, *Proc. Roy. Soc.*, 1903, 72, 204.

[12] Himstedt and G. Meyer, *Ann. Physik*, 1904, (iv.), 15, 184; *cf.* Giesel, *Ber.*, 1903, 36, 2299; 1906, 39, 2244.

[13] G. Martin, *Chem. News*, 1902, 85, 205.

should be 0·439 cu. mm. at N.T.P.: experimental determinations of the amount have given figures in good agreement with this result.[1] Since then its production during many other radioactive changes has been observed.[2]

The whole matter is one of great interest and importance. It has only been possible to give a mere outline of the chief facts here, and the reader who desires further information is referred to Soddy's *The Chemistry of the Radioactive Elements* (Longmans & Co, 1912), and the sections on Radioactivity in the *Annual Reports* of the Chemical Society, especially vol. vii. (1909), pp. 232 *et seq.*

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[1] See, *e.g.*, Dewar, *Proc. Roy. Soc.*, 1908, A, 81, 280.

[2] For example, from uranium and thorium in quantities of the same order as those calculated: *see* Soddy, *Phil. Mag.*, 1908, [vi.], 16, 513; *Physikal. Zeitsch.*, 1909, 10, 41.